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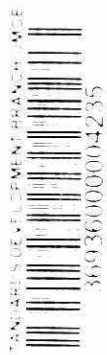

MINE WASTE CONTROL IN ONTARIO

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Ministry of the Environment

The Honourable
Harry C. Parrott, D.D.S.,
Minister

Graham W. S. Scott, Q.C.,
Deputy Minister

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MINE WASTE CONTROL

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THE PROBLEM OF ACID MINE DRAINAGE IN ONTARIO

by

John R. Hawley

A paper presented at the Third Annual Meeting
of the Canadian Mineral Processors
January 12, 20 and 21, 1971.

OTTAWA, Canada.

THE PROBLEM OF ACID MINE DRAINAGE IN ONTARIO

Even though acid mine drainage is an old problem, particularly in coal mining areas, its appearance in the form of a major environmental hazard in the hardrock mining districts of Ontario was unexpected. The yellow and amber coloured wastes that characterize an acid mine drainage situation were first noted by the Ontario Water Resources Commission in the uranium mining Elliot Lake district. Problems of a similar nature were also noted in the copper-lead-zinc camp at Manitouwadge, the nickel camp at Sudbury and at numerous isolated base metal properties, both in and out of the Province of Ontario.

Without exception, when acid mine drainage type effluents were evident, the specific companies involved worked sulphide or sulphide-associated ores. Without exception, the ore bodies contained quantities of iron sulphide (in various mineralogical forms) and, without exception, the milling circuits serving these operations were such that the iron sulphides were rejected to the tailings areas as waste.

Once in a tailings area and after a varying period of time, iron sulphides react to form water soluble salts which, when discharged in the effluents from the tailings area, can affect stream chemistry and stream ecology.

It is not unusual that the minerals pyrite, marcasite and pyrrhotite (all iron sulphides) react to form a stable oxide under atmospheric conditions. The law of stability of rocks and minerals, for instance, states that rocks and minerals are stable only in the environment of their formation and, as the environment surrounding them changes, the rocks and minerals tend to change to other species which are relatively more nearly stable under the conditions of the new environment (a). Under atmospheric conditions, iron oxide exhibits a greater stability than iron sulphide.

The basic reactions that describe the chemistry of an acid mine drainage situation are well known and are detailed here as a simple review (b):

Reaction #1 (Sulphide to Sulphate)

When natural sulphuritic material in the form of a sulphide (and usually in combination with iron) is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition:

(a) Assuming that the process takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of (water soluble) ferrous sulphate:

$$FeS_2 + 3\ O_2 \longrightarrow FeSO_4 + SO_2$$

(b) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapour), then the direct formation of sulphuric acid and ferrous sulphate in equal parts results:

$$2\ FeS_2 + 2\ H_2O + 7\ O_2 \longrightarrow 2\ FeSO_4 + 2\ H_2SO_4$$

In most mining environments (underground as well as in the tailings area), the above reaction is favoured.

Reaction #2 [Oxidation of Iron (Ferrous to Ferric)]

Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state to form (water soluble) ferric sulphate:

$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \longrightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Most evidence seems to indicate that a specific bacterium (T. ferrooxidans) is involved in the above reaction and is responsible for, at least, accelerating the oxidation of the ferrous iron to the ferric state.

Reaction #3 (Precipitation of Iron)

The ferric iron associated with the sulphate ion commonly combines with the hydroxyl $(OH)^-$ ion of water (HOH) to form ferric hydroxide. In an acid environment, ferric hydroxide is largely insoluble and accordingly precipitates:

$$Fe_2(SO_4)_3 + 6\ H_2O \longrightarrow 2\ Fe(OH)_3 + 3\ H_2SO_4$$

IMPORTANT NOTE:

The ferric ion can and does enter into an oxidation reduction reaction with iron sulphide whereby the ferric ion "backtriggers" the oxidation of further amounts of sulphuritic materials (iron sulphides, etc.) to the sulphate form thereby accelerating the acid-forming process:

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \longrightarrow 3\ FeSO_4 + 2\ S^o$$

$$S^o + 3\ O + H_2O \longrightarrow H_2SO_4$$

The fact that very little 'free' sulphuric acid is found in mine waste drainage is probably due to the reactions between other soluble mineral species and sulphuric acid.

The iron sulphides, of course, are not the only sulphides that find their way into the tailings areas. Mill recoveries are seldom greater than 97 percent and, as such, limited quantities of ore materials also become an integral part of the tailings mass. The ore materials are generally sulphides themselves (chalcopyrite, galena, sphalerite, etc.) and, therefore, enter into oxidation reactions that, in a simple sense, tend to resemble the iron sulphide oxidation reactions that have already been described.

When the correct conditions are presented, sulphide minerals in a tailings mass will oxidize to the corresponding

metal ions plus the sulphate ion. Generally speaking, the sulphate ion will leave the tailings area. The metal ions on the other hand, depending on many chemical factors, may be precipitated as 'insoluble' hydroxides, oxides, carbonates, sulphates or silicates, etc., and hence be retained within the tailings area or may be carried away in solution from the site of oxidation and hence leave the tailings area. Iron, copper, cobalt, manganese, zinc and nickel all form soluble salts (usually sulphates) under acid mine drainage conditions and are, therefore, commonly detected in the effluents from affected areas. Lead, on the other hand, forms a relatively insoluble sulphate (known as the mineral anglesite in geology texts) and is therefore only rarely detected in concentrations greater than 1 part per million under similar circumstances.

The factors that govern the rate of the geochemical destruction of the naturally occurring inorganic sulphides are essentially the same factors that govern the rate of any chemical reaction that takes place. However, each factor must be modified or amplified to suit the processes of nature. The single most important factor is probably available surface area. If the total available surface area of any substance that is subject to a chemical reaction is increased, the rate of reaction itself increases. It then seems to follow that, if the total surface area of a sulphide mass

is increased, the rate of the geochemical decomposition of that mass will also increase. As partial proof of this, consider sulphide orebodies which usually outcrop to a limited extent if at all. In many countries of the world, sulphide orebodies show signs of weathering to a depth of several hundred feet and indications of weathering to a depth of over one thousand feet have been recorded. This alteration at depth can only be explained by the apparent existence of secondary surfaces in the deposit. Secondary surfaces, commonly the result of unbalanced stresses and strains within a deposit are generally created mechanically and are given such names as faults, joints and torsion cracks, etc. As a result of faulting, etc., coupled on occasion with diverse solution effects, very sophisticated natural drainage networks can be set up within a particular deposit. The network can be so efficient, in fact, that a company working the deposit has to rely heavily on pumps to keep the workings dry. The water percolating through the deposit may bring oxygen, among other substances, into direct contact with the sulphide ore. The sulphide ore reacts to produce water soluble salts and sulphuric acid. The water that brought the oxygen to the ore also removes the soluble reaction products from the ore and thus permits the continuation of the reaction. When this solution gains

access to mine workings, it is generally characterized by a relatively low pH, a relatively high sulphate content and an abnormal concentration of the various heavy metals. In appearance, it may be clear and colourless or it may be coloured light-yellow, dark-yellow, amber or rusty orange. The vaious colours are due to the state of oxidation of the iron present. If, by chance, cemented backfill is used in the mine, the highly alkaline underflow from backfilled areas will perhaps mask (by neutralization) the original acid characteristics of the mine water but the acid situation within the deposit still exists nonetheless.

To relate this discussion to a tailings area is quite simple. A tailings area of the type we are discussing can be regarded as nothing more than a highly fractured sulphide 'ore body'. The enormous secondary surface area of the 'ore body' has been created mechanically as a result of crushing and grinding in the mill. Oxygen-carrying water has ultimate access to virtually every particle in the mass. It is only logical to suspect therefore that a tailings area that contains quantities of iron sulphide will (unless the gangue in the original ore has sufficient residual neutralizing capacity and this is generally not the case) produce phenominal quantities of water-soluble acid-producing salts.

Tailings areas that are well known as acid producers

within the Province of Ontario have been examined in detail. The iron sulphide content of these areas varies, so far, from a minimum of 2.5 percent to a maximum of 72 percent. Many other properties with sulphide contents within this range are known.

Iron sulphide occurs in three principal forms in the tailings areas of the Province:

(i) pyrite

(ii) marcasite

(iii) pyrrhotite

Pyrite is an isometric form of ferrous disulphide. Marcasite is also ferrous disulphide but is orthorhombic in nature. Pyrrhotite is a hexagonal form of ferrous sulphide that contains a slight excess of sulphur.

The rates of reaction of pyrite, marcasite and pyrrhotite under typical acid mine drainage circumstances are said to be significantly different. It has been reported (c), for instance, that marcasite reacts 9 times as fast as good quality pyrite. On the other hand, impure sulphide material (corresponding perhaps to poor quality pyrrhotite) is said to react up to 81 times as fast as good quality pyrite. These facts are interesting but they are really not too significant as far as the Ontario mining industry is concerned. Severe acid mine drainage problems are known to occur in Ontario where

marcasite and pyrrhotite are, relatively speaking, absent. In addition, most of the tailings areas in Ontario of the type we are discussing contain intimate mixtures of two or more iron sulphide species.

If sufficient care is taken during the years of conventional mine-mill operations, the inherent alkalinity of most flotation circuits plus perhaps minor lime additions should control any tendency towards an acid mine drainage situation where the main decant is concerned. However, during the same period, that is, the operational life of the mine-mill complex, there is a very good chance that the underflow (seepage) from the tailings area will gradually become highly acid in nature and will therefore require extensive chemical treatment if environmental standards are to be maintained. In fact, in the Province of Ontario, it is primarily the untreated seepage discharges from active tailings areas plus uncontrolled runoff and seepage from abandoned areas that gives rise to the undesirable waste discharges that we refer to as acid mine drainage.

Acid mine drainage in Ontario is cumulative. Abandoned properties will continue to produce 'acid' for decades. As the number of abandoned sulphide operations increases, the acid load that our environment must assimilate also increases. Thus this is a problem of immediate concern which

must be brought under effective control.

At the present time almost fifty square miles of the Province of Ontario are covered by active and abandoned tailings areas. For the most part, these tailings areas occupy depressions that at one time were the site of lakes or very wet swamps. When a lake is inundated with tailings, it does not disappear. It merely exists as a 'ghost' within the tailings mass and occupies the spaces between tailings particles. The watershed that fed the 'former' lake does not disappear either. It now feeds the tailings area. If the lake overflowed continuously before tailings deposition, it will overflow after tailings deposition. Generally, however, the overflow will not be noticeable until the tailings area is completely abandoned. We then call the overflow 'seepage'.

True seepage, that is water that has percolated a considerable distance through sulphide bearing tails, is by nature highly contaminated. Consider the following seepage sample from an abandoned tailings area in the Elliot Lake district:

pH	2.0
Sulphate as $SO_4^=$	7,440 ppm
Acidity as $CaCO_3$	14,600 ppm
Ferric Iron as Fe	1,450 ppm
Ferrous Iron as Fe	1,750 ppm

Uranium as U	7.2 ppm
Zinc as Zn	11.4 ppm
Nickel as Ni	3.2 ppm
Cobalt as Co	3.8 ppm
Copper as Cu	3.6 ppm
Manganese as Mn	5.6 ppm
Aluminum as Al	558 ppm
Lead as Pb	0.67 ppm
Cadmium as Cd	0.05 ppm
Lithium as Li	0.07 ppm
Vanadium as V	20 ppm
Silver as Ag	0.05 ppm
Titanium as Ti	15 ppm
Magnesium as Mg	106 ppm
Calcium as Ca	416 ppm
Potassium as K	69.5 ppm
Sodium as Na	920 ppm
Arsenic as As	0.74 ppm
Phosphorus as P	5.0 ppm
Chemical Oxygen Demand	270 ppm

The above sample, when taken, was clear, colourless and sparkling in appearance.

Once characteristic of true seepage flows is their inherent abnormal heavy metals content. The metals present and their relative concentrations vary from property to property. Metals in solution are always present and, therefore, in order to preserve our aquatic environment, the removal of these substances must form an integral part of any treatment process that is to be applied to this type of effluent or, indeed, to any of the effluents that arise from mining, milling and tailings disposal operations.

How do trace elements affect the stream ecology (d)? Toxic metals act in several ways. Salts of

electropositive metals such as silver, molybdenum, antimony, thallium and tungsten react with proteins and destroy metabolites essential to vital function. Some metals pervade the active sites of an enzyme and render it useless through substitution for the normal metal constituents. These metals are selenium and tellurium and, to a much lesser extent, beryllium. Precipitation and chelation of essential metabolites is the mode of toxic action shown by aluminum, beryllium, scandium, titanium, yttrium, zirconium, barium and iron. Catalytic decomposition of proteins is shown by lanthanum and other rare earths. A final mode of toxic action is reaction with the cell membrane to alter its transport properties. Salts of gold, cadmium, copper, lead and uranium show this action.

It is clear that the problem of acid mine drainage in the Province of Ontario must be eliminated or at least minimized in the very near future. How can this be accomplished?

When involved in an acid mine drainage situation, we propose ten basic rules that can be and should be considered:

Rule #1

Define the problem.

The average mine manager in today's world is

expected to be more than just a successful blend of engineer, geologist, metallurgist, chemist, physicist and economist. Now he is expected to be an ecologist.

On one hand the mine manager is harassed by the head office for spending too much on waste treatment; on the other hand, by the regulatory agencies for spending too little. At any rate, a mine manager can remove some of his worries concerning effluent treatment by simply knowing exactly what he is up against. He should have in his possession, for instance, a very detailed map of the property that he is responsible for. The map should indicate the source, direction and volume of all flows that enter and/or leave the property. Seepage flows from the tailings area should be accurately traced. A routine chemical analysis of each flow should be available. More important, a complete SCAN type analysis should be run at least once on all major flows from the property (a SCAN analysis is an analysis in which the chemist has attempted to identify and determine the amount of every contaminant in the flow).

When dealing with an acid mine drainage situation any analytical results should include pH, sulphates, acidity, iron, copper, zinc, cobalt, nickel, manganese and lead. In addition to the above, any SCAN type analysis should include

the following:

vanadium
cadmium
mercury
tin
titanium
chromium
molybdenum
barium
lithium
sodium
potassium
calcium
aluminum
arsenic
phosphorus

If any heavy metal exists in the effluent or effluents from the property in concentrations greater than 1.0 part per million, it should be regarded as a potential source of trouble. It may cause downstream environmental problems. If, on the other hand, several heavy metals (e.g. cobalt, copper, zinc and nickel) occur in the effluent or effluents in concentrations of less than 1.0 part per million but the combined total is greater than 1.0 part per million, the synergistic effect (one ion acting with another) may be (and probably is) great enough to warrant concern.

Rule #2

Do not ignore the preliminary signs of an acid mine drainage situation.

Acid mine drainage symptoms develop long before acid mine drainage becomes the dominant chemical force in

the tailings area. These symptoms are best observed in relatively small non-fluctuating seepage flows that emerge from the base of tailings dams on a property.

First the sulphate concentration begins a lazy climb upwards. This can generally be detected by periodic sampling of the same flow over a number of months. The tailings area decant should not be chosen for this type of work since sulphate additions in the mill, which tend to increase as production increases, make the establishment of a base sulphate concentration quite difficult. Also, the decant is fed by wastes that originate in the mill, run across the top of the tailings mass and then leave the area. Seepage, on the other hand, is a result of water percolating through a tailings mass and is therefore in a better position to pick up soluble oxidation products.

Since the sulphate concentrations of most natural lakes, rivers and streams in northern Ontario is approximately 10 parts per million a reading of a few hundred parts per million sulphate in a seepage flow is cause for concern. Readings of 1,000 parts per million sulphate are very common when acid mine drainage conditions are well established. Seepage flows containing in excess of 11,000 parts per million sulphate have been noted in the Elliot Lake district.

An increase in sulphate content usually coincides with a decrease in pH and an increase in the concentration of iron and other heavy metals.

When the pH drops to approximately 3.0, the situation becomes critical for reasons discussed later in this paper. Once the pH of the affected portions of the tailings mass drops below 3.0, the situation is practically irreversible and treatment costs become enormous.

Rule #3

Collect all effluents from a specific property at a common point for treatment before discharge to a watercourse.

Quite commonly, an acid mine drainage problem at a specific property is magnified in the eyes of the public by the simple fact that wastes are discharged not to one watercourse but to several. Most operations, of course, utilize one or more decant structures that discharge to a common depression, stream, or lake. However, what has been forgotten is that seepage flows which are generally low-volume highly contaminated untreated flows, discharge from the base of almost every dam on the property. One or more of these flows will probably discharge into a stream or lake that is not related to the watercourse receiving the decant overflow. The result is the potential for impairment

of two or more watercourses instead of one. Furthermore, two treatment systems would be required instead of one.

Rule #4

Do not mishandle raw seepage flows.

Raw (untreated) seepage flows usually contain excessive quantities of both ferrous and ferric sulphate - especially when the pH drops below 3.0 (a common occurrence). Reaction #3 in the iron sulphide oxidation sequence given previously in this paper states:

> "The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion 'backtriggers' the oxidation of further amounts of sulphuritic materials (iron sulphides etc.) to the sulphate form thereby accelerating the acid-forming process:
>
> $Fe_2(SO_4)_3 + FeS_2 + H_2O \longrightarrow 3\ FeSO_4 + 2\ S^o$
>
> $S^o + 3\ O + H_2O \longrightarrow H_2SO_4$."

Therefore, under no circumstances, should untreated seepage be collected and pumped back onto a tailings area. This is as close to 'acid mine drainage suicide' as a mine manager can possibly get. On the other hand, raw seepage can be collected and treated (neutralized) with lime (to a pH of 8.5) and then returned to the tailings area. This practice is acceptable but is still not advisable. Seepage

flows are maintained, in part, by water ponding on the tailings area. Thus, by returning seepage, treated or untreated, to the tailings area the problem is aggravated.

Rule #5

Use the forces of nature for acid mine drainage treatment whenever and wherever possible.

Characteristically, seepage flows that originate within a sulphidic tailings mass tend to change colour on standing while exposed to the atmosphere. Initially clear and colourless the waste assumes a faint yellow flush which, in time, gradually deepens to an intense amber-red. This latter colour is due to very finely divided suspended particles of hydrous ferric oxide ($Fe_2O_3.nH_2O$).

Ferrous iron is quite commonly found as a component of acid seepage flows and, in Ontario, occasionally represents over 50 percent of the iron species present. If a flow contains a relatively high ferrous to ferric ratio, we term the flow 'immature'. If the ferrous to ferric ratio is low, the flow is termed 'mature'. Obviously, as the ferrous iron in any flow oxidizes, the ferrous to ferric ratio decreases and the flow itself matures. Thus, highly coloured flows tend to be mature flows; colourless flows tend to be immature flows.

Fortunately (e) the potential of the Fe^{3+} - Fe^{2+}

(ferric-ferrous) couple, 0.771 volts, is such that molecular oxygen can convert ferrous iron to ferric iron in acid solutions.

$$2\ Fe^{2+} + \tfrac{1}{2}\ O_2 + 2\ H^+ = 2\ Fe^{3+} + H_2O$$

$$E^o = 0.46 \text{ volts}$$

In a basic solution, of course, the oxidation process is still more favourable:

$$\tfrac{1}{2}\ Fe_2O_3.3\ H_2O + e = Fe(OH)_2 + (OH)^-$$

$$E^o = -0.56 \text{ volts}$$

Neutral and acid solutions of ferrous iron oxidize less rapidly with increasing acidity (despite the fact that the potential of the oxidation reaction will become more positive).

The oxidation of ferrous to ferric species by molecular oxygen appears to involve the initial formation of an ion FeO_2^{2+}. The reaction kinetics also suggest that a binuclear species is a transient intermediate formed by the attack of Fe^{2+} on FeO_2^{2+}. The overal reaction of

$$FeO_2^{2+} + Fe(H_2O)^{2+} \longrightarrow Fe(OOH)^{2+} + Fe(OH)^{2+}$$

leads to the hydroperoxo ion which rapidly decomposes to give Fe^{3+} and HO_2^-, which itself either oxidizes Fe^{2+} or decomposes to O_2.

One of the most conspicuous features of ferric iron (which all seepage flows of the type we are discussing

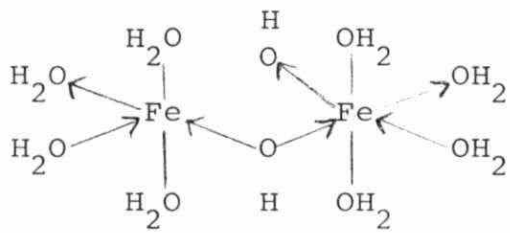
contain) in aqueous solution is its tendency towards hydrolysis and/or formation of complexes. It has been established that the hydrolysis is governed in its initial stages by the following equilibria constants:

$$\left[Fe(H_2O)_6\right]^{3+} = \left[Fe(H_2O)_5\ (OH)\right]^{2+} + H^+ \qquad K = 10^{-3.05}$$

$$\left[Fe(H_2O)_5\ (OH)\right]^{2+} = \left[Fe(H_2O)_4\ (OH)_2\right]^{+} + H^+ \qquad K = 10^{-3.26}$$

$$2\left[Fe(H_2O)_6\right]^{3+} = \left[Fe(H_2O)_4\ (OH)_2\ Fe(H_2O)_4\right]^{4+} + 2H^+ \qquad K = 10^{-2.91}$$

In the last of the above equations, the binuclear species is written to imply the structure



which, though plausible, is quite unproved.

From the constants for these equilibria, it can be seen that even at the rather acid pH's of 2-3 (most acid seepage flows fall within or close to this range) the extent of hydrolysis is very great and, in fact, in order to have solutions containing ferric ion mainly (say approximately 99 percent) in the form of the pale purple hexaquo ion, the pH must be around zero. As the pH is raised above 2-3, more highly condensed species than the binuclear one noted above are formed. Attainment of equilibrium becomes sluggish and colloidal gels are formed. Ultimately, hydrous

ferric oxide is precipitated. There is no evidence to suggest that any definite hydroxide, $Fe(OH)_3$ exists and the reddish-brown precipitate commonly called ferric hydroxide is best described as hydrous ferric oxide, $Fe_2O_3.n\ H_2O$.

The various hydroxo species, such as $\left[Fe(OH)\ (H_2O)_5\right]^{2+}$ are yellow in colour because of charge transfer bands in the ultraviolet which have tails coming into the visible. Thus aqueous solutions of ferric salts even with non-complexing anions are yellow unless extremely acid. As colloidal hydrous ferric oxide accumulates the colour of the 'solution' will change to amber-brown and, under unusual circumstances, to deep blood-red.

The fact that seepage waste does generally turn colour on standing and the fact that advanced inorganic chemistry texts indicate that favourable reactions can occur spontaneously led us to believe that one method of partially treating seepage waste involving essentially no reagent costs would be the simple ponding of such wastes. After two and one-half years study in the Elliot Lake district, we have concluded that such a method of pretreatment is both feasible and practical.

The cost of lime that is required to effectively

neutralize (to a pH of 8.5) most seepage flows is prohibitive. Most of the lime (or NaOH, etc.) in this type of reaction is consumed not in reactions with free acid but in reactions with soluble (metal) salts (see Figure 3). This is all very well as the metals have to be removed in order that water quality standards can be met. However, any free acid that remains after metal precipitation still must be neutralized. The presence of a little free acid can cause a tremendous pH depression.

Natural ponding, inefficient as it may be, under the proper conditions will result in up to 50 percent reductions in metal and sulphate concentrations (effluent as opposed to influent). This, of course, represents a significant saving in neutralizing reagent costs.

Efficient ponding can be accomplished if the following conditions are satisfied:

(a) The retention time (the time the waste is held in the pond) must be as great as possible (in the order of months rather than days).

(b) The pond should be as shallow as possible (to enhance oxygen transfer from the atmosphere).

(c) The pond waste should not be allowed to come into contact with tailings containing iron sulphides (see Rule #4).

(d) Wastes being decanted from the pond should be taken from the pond surface (preferably a sluice type overflow, etc.). The surface film of the pond is the zone of maximum oxidation and should therefore contain less unoxidized material than the waste a foot or so below the surface.

This type of seepage pretreatment facility can be set up in any swampy ravine or depression on the property. A crude low earth or log dam, a large beaver pond or a small stagnant pot-hole lake in the vicinity of the operation is all that is required. However, please note Rule #3. The overflow from this type of pretreatment facility should be directed to the area that receives the main decant overflow. In some cases, the residual alkalinity of the decant (providing, of course, that the decant itself is alkaline) may be all that is required for final seepage treatment.

The trace heavy metals that we have already discussed respond dramatically to this type of pretreatment. Reductions, in some cases, of up to 90 percent have been noted.

Again, may we stress that this type of pretreatment is designed for seepage flows and it must not be carried out in contact with iron sulphide bearing tails.

By now you may have realized that, although all seepage flows on any particular property should be combined before final discharge (see Rule #3), each individual flow can be treated by itself in any convenient depression. The overflow from each depression could then be directed to a common area where final treatment can take place.

Since acid mine drainage situations do generally not reach a peak until after the individual properties have been abandoned and since treatment must continue especially on abandoned properties, it is wise to avoid mechanical pumping wherever possible. A gravity flow which, on occasion, is more expensive to install at the outset, will be more economical in the long run.

Rule #6

Make the maximum possible use of required water resources.

Acid mine drainage is more than just a problem of specific contaminants. It is a problem of volume. Most operations, for instance, would have no difficulty in adequately treating 8,000 gallons per day of typical acid mine drainage waste. But the treatment of 800,000 gallons per day would be a different matter. It is, perhaps, almost economically impossible under most circumstances.

The most effective way to minimize an overall acid

they imply. Seepage losses are usually great and as a result may cause a slow down the build-up of various

mine drainage problem during the years of conventional mine-mill operations is to reduce the total volume of

$$K_{sol}\ Fe(OH)_3 = \left[Fe^{+3}\right] \left[(OH)^{-}\right]^3$$

therefore:

Solubility of $Fe(OH)_2$ and $Fe(OH)_3$ from K_{sol} at 25° C

$K_{sol}\ Fe(OH)_2 = 5.25 \times 10^{-14}$

$K_{sol}\ Fe(OH)_3 = 1 \times 10^{-38}$ (also 10^{-40} is reported)

pH	Fe^{+2}, ppm	Fe^{+3}, ppm
1		56,000
2		560
3		0.56
4		0.00056
5		
6	29,400	
7	294	
8	2.94	
9	0.0294	

Ferrous Iron

Equilibrium composition for the system Fe^{+2} - $Fe(OH)_2$ at various pH values expressed as a faction of the total Fe^{+2} present.

pH	5.0	6.0	6.5	7.0	7.5	8.0	9.0
Fe^{+2}	0.999	0.903	0.485	0.087	0.0094	0.00095	0.00001

Ferric Iron

Equilibrium composition for the system Fe^{+3} - $Fe(OH)_3$ at various pH values expressed as a faction of the total Fe^{+3} present.

pH	1.00	1.25	1.50	1.75	2.00	3.00
Fe^{+3}	0.8677	0.1947	0.0979	0.0213	0.0085	0.000008

The distribution of Fe^{+2} and $Fe(OH)_2$ as a function

By now you may have realized that, although all seepage flows on any particular property should be combined before final discharge (see Rule #3), each individual flow can be treated by itself in any convenient depression. The overflow from each depression could then be directed to a common area where final treatment can take place.

Since acid mine drainage situations do generally not reach a peak until after the individual properties have been abandoned and since treatment must continue especially on abandoned properties, it is wise to avoid mechanical pumping wherever possible. A gravity flow which, on occasion, is more expensive to install at the outset, will be more economical in the long run.

Rule #6

Make the maximum possible use of required water resources.

Acid mine drainage is more than just a problem of specific contaminants. It is a problem of volume. Most operations, for instance, would have no difficulty in adequately treating 8,000 gallons per day of typical acid mine drainage waste. But the treatment of 800,000 gallons per day would be a different matter. It is, perhaps, almost economically impossible under most circumstances.

The most effective way to minimize an overall acid

mine drainage problem during the years of conventional mine-mill operations is to reduce the total volume of effluent that leaves the property. The most convenient way to reduce the total volume of effluent leaving the property is to set up the mine-mill complex on the basis of total or at least partial water recirculation.

We all realize, of course, that the re-use of water in most mine-mill operations is not as easy as it sounds. Flotation circuits, for instance, are noted for their extreme sensitivity. Even the simple re-use of underground (or open pit) mine water in the grinding circuit of a mill that employs normal froth flotation circuits can theoretically cause problems if the water contains significant quantities of organic materials such as oil. The occurrence of trace quantities of oily materials in underground mine water as a result of mining operations is not only possible but is probable. If oil is expected to be a problem at any operation, then all underground water should be pumped to a convenient depression on the surface near the mill. In the depression, oily materials will tend to separate and rise to the surface. Water, for re-use, should be taken from below the surface of this pond. If underground mine water is to be re-used in any mill that employs a froth flotation

circuit, water soluble or emulsified oils should not be used underground. This type of oil will not easily respond to simple ponding.

With regard to underground mine water, the OWRC is recommending that all underground (or open pit) mine water be directed to the grinding circuit of the mill for re-use.

The recirculation of a tailings area decant involves even more than does the simple re-use of underground mine water. The tailings area decant can and often does contain residual quantities of the more persistent milling reagents. If the decant, therefore, is indiscriminately recirculated to the mill, the mill operator can lose partial control of the flotation process. The ensuing concentrate losses are serious not only from an economic standpoint but also from the standpoint that a portion of a non-renewable natural resource has been lost. On the other hand, if the discharge of contaminated decant wastes alters or destroys the life support properties of a watercourse or a watershed, the ultimate consequences may be even more far reaching.

Total recirculation systems are seldom what they imply. Seepage losses are usually great and as a result may cause a slow down the build-up of various

dissolved solids in the recirculated liquid. In addition, most total recirculation systems require a decant bleed-off from time to time in order to control the dissolved solids content. This decant discharge must be chemically treated before it can be released to a watercourse.

The mining industry of Ontario is fortunate to have an extemely competent group of mining reagent suppliers. These people have demonstrated an interest not only in the efficiency of their products but also in the effects of their products on the mine worker and on the mine environment.

Close working cooperation is necessary between the various government agencies, the mine reagent suppliers and the mine operators to achieve a satisfactory solution to all the problems of wastewater recirculation. It is probable, for environmental reasons alone, that every mining operation in the Province of Ontario will be utilizing complete water recirculation systems by the end of this decade.

Rule #7

Do not needlessly contaminate unrequired water resources.

Under no circumstances should fresh water be permitted to gain access to a suphide-bearing tailings

area. All reasonable efforts should be made to divert streams and large springs around a tailings area or away from a tailings area. Once in a tailings area, fresh water tends to pick up quantities of acid-producing water soluble salts, etc. The result is that chemical treatment is required for water that is not needed in the mine-mill process. The real significance of this factor is generally acknowledged only after the property has been abandoned and profit-consuming waste treatment facilities must continue to be operated.

Excess water on a tailings area, particularly an abandoned tailings area, helps to maintain undesirable seepage flows and may heighten problems of instability of embankment structures.

Rule #8

Maintain the pH of all effluents at a level which will ensure the optimum precipitation of all metals including iron.

The overall solubility of Fe^{+2} and Fe^{+3} in mine water (f) is determined by many factors, none of which can be evaluated as an isolated variable. However, for both Fe^{+2} and Fe^{+3} the limiting solubility at any pH is the solubility satisfying the equations:

$$K_{sol}\ Fe(OH)_2 = \left[Fe^{+2}\right] \left[(OH)^-\right]^2$$

and

$$K_{sol}\ Fe(OH)_3 = \left[Fe^{+3}\right] \left[(OH)^-\right]^3$$

therefore:

Solubility of $Fe(OH)_2$ and $Fe(OH)_3$ from K_{sol} at 25° C

$K_{sol}\ Fe(OH)_2 = 5.25 \times 10^{-14}$

$K_{sol}\ Fe(OH)_3 = 1 \times 10^{-38}$ (also 10^{-40} is reported)

pH	Fe^{+2}, ppm	Fe^{+3}, ppm
1		56,000
2		560
3		0.56
4		0.00056
5		
6	29,400	
7	294	
8	2.94	
9	0.0294	

Ferrous Iron

Equilibrium composition for the system Fe^{+2} - $Fe(OH)_2$ at various pH values expressed as a faction of the total Fe^{+2} present.

pH	5.0	6.0	6.5	7.0	7.5	8.0	9.0
Fe^{+2}	0.999	0.903	0.485	0.087	0.0094	0.00095	0.00001

Ferric Iron

Equilibrium composition for the system Fe^{+3} - $Fe(OH)_3$ at various pH values expressed as a faction of the total Fe^{+3} present.

pH	1.00	1.25	1.50	1.75	2.00	3.00
Fe^{+3}	0.8677	0.1947	0.0979	0.0213	0.0085	0.000008

The distribution of Fe^{+2} and $Fe(OH)_2$ as a function

of pH is graphically illustrated in Figure 1. Similarly, the distribution of Fe^{+3} and $Fe(OH)_3$ as a function of pH is illustrated in Figure 2.

Figure 2 indicates that the ferric ion cannot exist, as such, in a solution having a pH much greater than 3.0. It must revert to a hydroxide-type form. Limited amounts of ferrous iron, however, can exist in solution at a pH of 8.0 (as indicated by figure 1). If a decant is maintained at a pH of 5.0 ferric iron in the overflow will be largely in the form of the relatively harmless hydroxide. However, it is possible that small quantities of ferrous ion will also exist in the overflow and hence leave the tailings area. If the ferrous ion is associated with the sulphate ion (as it usually is), then downstream oxidation will give rise to ferric sulphate that will hydrolyze to form ferric hydroxide and sulphuric acid. The probable result would then be a downstream pH depression. The downstream pH depression, of course, would create conditions whereby the ferrous ion could migrate even farther downstream and so on until a natural balance between the amount of acid being produced and the alkaline characteristics of the downstream environment was reached.

Obviously, if an operation is discharging an effluent at a pH of 7.5 and downstream pH problems are being

encountered, not enough neutralizing agent is being added.

At a pH of 8.0 (necessary to meet the requirements of iron), many heavy metals do not precipitate to the extent that the resulting effluent can meet water quality standards. At a pH of 8.5, however, most problems are overcome. If undesirable quantities of specific metals (Zn, Ni, Mn, etc.) still remain in solution, the pH must be further increased.

Figures 1 and 2 indicate that at pH values less than 3.0 significant quantities of both ferrous and ferric iron can co-exist in solution and hence the acid mine drainage process becomes very efficient. Masses of hydroxides do not clog up oxidation sites or block solution passageways. Unfortunately, as the pH drops below 3.0, ideal conditions are set up for a bacterial attack on the sulphides. Once this attack is firmly established, the acid mine drainage process is practically irreversible.

Rule #9

Do not ignore the action of the wind on a tailings area.

Deflation (g) is by far the most important work of the wind and its significance can scarcely be over estimated. The lifting of material from a land surface is

largely the work of eddies and irregularities of movement of the wind, including many conflicting cross-currents.

The most important are, of course, the eddies of whirlwinds and tornadoes but many minor currents, due in part at least to the irregularities of the surface, are active in lifting the dust and fine sand. The ordinary convection currents of the atmosphere carry this finer material up to great heights. The force, which moves the particle, is due to the direct impact of the wind, plus the friction along its surface. The force of the direct impact varies with the velocity of the wind, and for a given velocity with the cross-section of the particle in the plane perpendicular to the direction of the wind, as well as with the orientation of the particle and it is of course most efficient when a smooth plane is opposed to the wind. The resistance of the particle varies with its mass, i.e., its size and specific gravity and to some extent, its form. In general, the velocity of the wind necessary to carry a spherical particle of given specific gravity varies as the square of the radius and conversely, the radius of a particle which can be supported by wind varies as the square root of the velocity. It was found that a uniform upward current of air will keep suspended quartz grains, the size of which varied with the velocity,

as follows:

Velocity in meters per second	Diameter of quartz grain in mm
0.50	0.04
1.00	0.08
2.00	0.16
3.00	0.25
4.30	0.35
5.00	0.41
6.00	0.49
7.00	0.57
8.00	0.65
9.00	0.73
10.00	0.81
11.00	0.89
12.00	0.97
13.00	1.05

From this, the formula $V = Kr$ was deduced, where K is a constant for the conditions of experiment and r the radius of the particle.

As a result of numerous measurements, the conclusion reached was that the average largest size of quartz particles that can be sustained in the air by ordinary strong winds is about 0.1 mm in diameter but the largest particle that can be transported (not held in suspension) is nearer 2 mm in diameter. This represents the limit of ordinary deflation.

The following table gives the approximate size of quartz sand grains moved by varying wind velocities.

Strength of wind in meters per second	Maximum diameter of sand grains in mm
4.5 - 6.7	0.25
6.7 - 8.4	0.5
9.8 - 11.4	1.0
11.4 - 13.0	1.5

These results are only approximate.

Problems due to wind blown tailings have been encountered at nearly every mining camp in Ontario.

Take, for example, the situation at Mine X. A large unbroken expanse (300 acres) of dry sulphidic tailings was exposed to the action of the wind. During the summer of 1968, it became apparent that swampy areas and "pot-hole" lakes located in the vicinity of the tailings area were contaminated although no normal link to the tailings area could be established. The colour changes in these waters were observed to be identical to the colour changes taking place in waters that were directly exposed to the tailings and, therefore, the possibility of the aerial transport of finely divided tailings from the tailings area to the waters in question could not be ignored.

The first step in our preliminary investigation of the airborne tailings was to secure a sample of tailings that we knew had already undergone some degree of aerial transport. Since deposits of wind-blown sand were easily recognizable and readily available in and around the tailings area, we selected this as our sample source.

The following are the actual average analytical

results of the samples in question:

Total iron as Fe	-	2.05%
Calcium as Ca	-	0.013%
Sodium as Na	-	0.006%
Potassium as K	-	0.316%
Phosphorus as P	-	0.033%
Aluminum as Al	-	0.68%
Titanium as Ti	-	0.046%

The above values were obtained by leaching the sample and therefore represent the material available to the natural processes of chemical decomposition and reaction. The iron content is, quite unexpectedly, very high. The bulk of the sample was composed of silicon dioxide (an "inert" material in this context).

A sieve analysis was also run on the wind-blown samples and serves, at least, to identify the size fractions that can be moved by the wind at this mining property:

	Retained by No. 10 mesh -	0.021%
Passed by No. 10,	Retained by No. 25 mesh -	0.029%
Passed by No. 25,	Retained by No. 45 mesh -	1.47%
Passed by No. 45,	Retained by No.100 mesh -	85.3%
Passed by No.100,	Retained by No.200 mesh -	11.7%
Passed by No.200 mesh		1.44%

Assuming that the samples were representative, it is immediately apparent that particles that will not pass through a 45 mesh screen (U.S. Standard Sieve) are generally too large to be subject to aerial transportation. On the other hand, particles that are small enough to pass

through a 45 mesh screen will undergo active aerial transportation should the required conditions present themselves.

It is necessary to point out that the above sieve analysis reflects the characteristics of the wind-blown deposits after they have undergone some degree of aerial transport. In other words, we have to assume that most of the fine (-200 mesh) material was removed by wind action from the deposits before we sampled them.

Analysis of the residual -200 mesh fraction revealed that it contained 15.2 percent iron as Fe. In other words, the fine dust that is blown from the tailings area and that eventually settles on the land and in the stagnant lakes and streams in the immediate area could possibly have contained up to 30 percent sulphides.

Many common methods, including revegetation and the use of artificial windbreaks, are known by which wind erosion can be controlled. As such, no further discussion is required.

Rule #10

Revegetate abandoned tailings areas and the downstream slopes of all tailings dams whenever and wherever possible.

A well-developed continuous cover of vegetation on abandoned tailings areas and on the downstream slopes

of all dams will ensure, to some degree, regulation of the effects of natural precipitation. Runoff, for all intents and purposes, will be eliminated. The volume of some seepage flows will be significantly reduced. The effects of the wind will be negligible. The area will blend into the surrounding landscape.

Recent legislation of the Ontario Department of Mines and Northern Affairs requires the "rehabilitation of tailings disposal and plant areas". Since it must be done, it may as well be done in such a manner that the problems of acid mine drainage are lessened.

In this paper, we have outlined the basic factors that are involved in the formation of acid mine drainage in the Province of Ontario. The chemical reactions responsible for acid mine drainage have been confirmed not only in Ontario but in other Provinces and in other countries.

It must be recognized that, while the basic problem of acid mine drainage is a common one, the extent of the problem and the factors causing the problem vary from property to property. For this reason, the solution to any particular problem of acid mine drainage depends largely on local circumstances. The goegraphy of the property and the composition of the ore and country rocks

are extremely important.

The rules that we have presented should be considered in special detail before the construction of a mine, a mill or a tailings area actually commences. When dealing with an existing problem of acid mine drainage, these rules should be applied whenever and wherever possible.

We are confident that the general implementation of these rules by the mining industry of Ontario would result in the virtual elimination within the Province of the problem known as 'acid mine drainage'.

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ASPECTS OF ACID MINE DRAINAGE IN SULPHIDE MINING AREAS

by

John R. Hawley

An article published by
"The Northern Miner", Spring 1971.

In coal mining areas, acid mine drainage is an old and well-known problem. In sulphide mining areas, the problem is new and was somewhat unexpected.

Pyrite, a common disulphide of iron, was found to be the cause (or source if you wish) of acid mine drainage in coal mining areas. Pyrite, in a finely divided state and in direct or indirect contact with our atmosphere, undergoes a process of chemical decomposition. Many of the products of decomposition are water soluble and have an ability to affect stream chemistry and ecology.

The basic reactions that describe the chemistry of an acid mine drainage situation are well-known and are detailed here simply as a review:

Reaction #1 - (Sulphide to Sulphate)

When pyritic material is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition.

(a) Assuming that the reaction takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of (water soluble) ferrous sulphate:

$$FeS_2 + 3\ O_2 \longrightarrow FeSO_4 + SO_2$$

(b) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapour),

then the direct formation of sulphuric acid and ferrous sulphate in equal parts results:

$$2FeS_2 + 2H_2O + 7O_2 \text{ -----> } 2FeSO_4 + 2H_2SO_4$$

In most mining environments (underground as well as in the tailings area), the above reaction is favoured.

Reaction #2 - (Oxidation of Iron-Ferrous to Ferric)

Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state to form (water soluble) ferric sulphate:

$$4FeSO_4 + 2H_2SO_4 + O_2 \text{ -----> } 2Fe_2(SO_4)_3 + 2H_2O$$

Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Most evidence seems to indicate that a specific bacterium (T. ferrooxidans) is involved in the above reaction and is responsible for, at least, accelerating the oxidation of the ferrous iron to the ferric state.

Reaction #3 - (Precipitation of Iron)

The ferric iron associated with the sulphate ion commonly combines with the hydroxyl $(OH)^-$ ion of water (HOH) to form ferric hydroxide. In an acid environment, ferric hydroxide is largely insoluble and accordingly precipitates:

$$Fe_2(SO_4)_3 + 6H_2O \text{ -----> } 2Fe(OH)_3 + 3H_2SO_4$$

Important Note

The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion "backtriggers" the oxidation of further amounts of pyritic materials to the sulphate form thereby accelerating the acid-forming process:

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \text{ -----} \rightarrow 3FeSO_4 + 2\ S^o$$

$$S^o + 3\ O + H_2O \text{ ----------} \rightarrow H_2SO_4$$

In Ontario, when acid mine drainage type effluents were evident, the specific companies involved worked sulphide or sulphide-associated ores. The related ore bodies contained quantities of iron sulphide (in various mineralogical forms) and the milling circuits, serving these operations, were such that the iron sulphides were rejected to the tailings areas as waste. Once in the tailings areas and after varying periods of time, the iron sulphides began to break down chemically. Acid mine drainage was the result.

When present, iron sulphide occurs in three principal forms in most tailings areas:

(1) pyrite
(2) marcasite
(3) pyrrhotite

Pyrite is an isometric form of ferrous disulphide. Marcasite is also ferrous disulphide but is orthorhombic

in nature. Pyrrhotite is a hexagonal form of ferrous sulphide that contains a slight excess of sulphur.

The rates of reaction of pyrite, marcasite and pyrrhotite under typical acid mine drainage circumstances are significantly different. Generally, however, most tailings areas contain intimate mixtures of two or more iron sulphide species. In addition, severe acid mine drainage problems are known to occur in Ontario where the most reactive species (marcasite and pyrrhotite) are, relatively speaking, absent.

Tailings areas that are well-known as acid producers within the Province of Ontario have been examined in detail. The iron sulphide content of the areas studied varied from a minimum of 2.5 percent to a maximum of 72 percent. Many properties with sulphide contents within this range are known.

The iron sulphides, of course, are not the only sulphides that find their way into the tailings areas. Mill recoveries are seldom greater than 97 percent and, as such, limited quantities of ore materials also become an integral part of a tailings mass. The ore materials are generally sulphides themselves (chalcopyrite, sphalerite etc.) and, therefore, enter into oxidation reactions that, in a simple sense, tend to resemble the iron sulphide

oxidation reactions that have already been described.

When the correct conditions are presented, sulphide minerals in a tailings mass will oxidize to the corresponding metal ions plus the suphate ion. Iron, copper, cobalt, manganese, zinc and nickel, for instance, all form soluble salts (usually sulphates) under acid mine drainage conditions and are, therefore, commonly detected in the flows from affected areas. Lead, on the other hand, forms a relatively insoluble sulphate (known as the mineral anglesite in geology texts) and is, therefore, only rarely detected in concentrations greater than 1 part per million under similar circumstances.

A tailings area of the type we are discussing can be regarded as nothing more than a highly fractured sulphide 'ore body'. The enormous secondary surface area of the 'ore body' has been created mechanically as a result of crushing and grinding in the mill. Oxygen-carrying water has ultimate access to virtually every particle in the mass. It is only logical to suspect therefore that a tailings area that contains quanities of iron sulphide will (unless the gangue in the original ore has sufficient residual neutralizing capacity and this is generally not the case) produce large quantities

of water-soluble acid-producing salts.

Acid mine drainage is a waste that is characterized by:

(1) a relatively low pH;

(2) a relatively high sulphate content;

(3) a relatively high iron content;

(4) the presence of an abnormal concentration of many metals such as manganese, nickel, cobalt, zince and copper.

(5) a tendency to change colour on standing (clear and colourless to yellow to deep amber red).

Many metals have been detected in undesirable concentrations in acid mine drainage type effluents and treatment for the removal of these metals must be provided. The absolute extent to which these metals affect the aquatic environment is currently being determined.

The main sources of the metals in the water leaving a pyritic tailings area are the iron sulphides themselves and not the associated ore sulphides. Several metals (e.g. nickel and cobalt) can substitute for iron in the iron sulphide lattice. Hence nickelian and cobaltian varieties of pyrite are known. When the pyrite breaks down in the above cases, nickel and cobalt got into solution. Spectroscopic traces of vanadium,

molybdenum, chromium, tungsten and thallium have all been reported in pyrite. Copper is also commonly recorded but is presumably due to microscopic impurities (inclusions, etc.) in the pyrite mass itself.

The ore sulphides do break down slowly and are the major source of many of the less well-known metal species that go into solution. However, the total contribution of the ore sulphides to the severity of the overall acid mine drainage situation is, at the present time, not well known.

If sufficient care is taken during the years of conventional mine-mill operations, the inherent alkalinity of most flotation circuits plus perhaps minor lime additions should control any tendency towards an acid mine drainage situation where the main decant is concerned. However, during the same period, that is, the operational life of the mine-mill complex, there is a very good chance that the underflow (seepage) from the tailings area will gradually become highly acid in nature and will, therefore, require extensive chemical treatment if environmental standards are to be maintained. In the Province of Ontario, the primary cause of downstream acid mine drainage problems relating to a specific operation has been found to be the untreated seepage discharges

from active tailings areas plus uncontrolled runoff and seepage from abandoned areas.

Acid mine drainage is cumulative. Abandoned properties will continue to produce 'acid' for decades. As the number of abandoned sulphide operations increases, the acid load that our environment must absorb also increases. Considering that, at the present time, almost fifty square miles of the Province of Ontario are covered by active and abandoned tailings areas and considering that a very healthy percentage of these areas are pyritic in nature, we can easily see that the problem facing the mining industry is significant in terms of environmental control.

While the basic problem of acid mine drainage is very common, the extent of the problem and the factors causing the problem vary from property to property. For this reason, the solution to any particular problem of acid mine drainage depends largely on local circumstances. Of extreme importance is the composition of the ore, the composition of the country rock and the geography of the property.

"ASPECTS OF THE PROBLEM OF ACID MINE DRAINAGE IN THE PROVINCE OF ONTARIO"

by

John R. Hawley

A Paper Presented at the
18th Ontario Industrial Waste Conference
Niagara Falls, Ontario
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Introduction

The rapid industrial development and utilization of natural resources in the Province of Ontario has presented many problems concerning our water environment. A tremendous upsurge in mining exploration and development in the past two decades plus uncorrected situations having origins in the mining activities of the early part of this century have resulted in serious deterioration of the quality of the water in many watersheds of the north where mining operations are carried out.

Acid mine drainage is a major environmental problem in Ontario's hardrock mining districts. Curiously enough, most specific acid mine drainage problems are not the result of indiscriminate hardrock mining activity but, instead, form a condition of it. The problem may occur whenever an orebody containing iron sulphides is exposed to the atmosphere.

The problem of acid mine drainage is not unique to Ontario. It is well known in other Provinces, the United States, Europe and Japan. In fact, acid mine drainage probably occurs on a worldwide basis.

The problem of acid mine drainage in Ontario begins when a mine-mill operation, during the processes of ore comminution and beneficiation, discards, as waste,

the various iron sulphide minerals that occur naturally in the ore. These iron sulphides, finely divided as a result of milling operations, are, along with other gangue (non-valuable) materials discharged as a slurry to a natural or man-made settling basin that is commonly referred to as a tailings area. Here, the slurry undergoes a natural solid-liquid separation and, under ideal conditions, the solid particles, including the iron sulphide minerals, are retained within the confines of the tailings area. The clarified liquid escapes the area via a structure called the decant and as seepage through the bases of permeable dams.

Once in a tailings area and after a varying period of time, the iron sulphide minerals react to form water soluble salts which, when discharged in the effluent from a tailings area, can affect stream chemistry and stream ecology.

The Chemistry of Acid Mine Drainage

This paper deals exclusively with the type of acid mine drainage problem that results when naturally occurring inorganic sulphides undergo spontaneous decomposition. The basic reactions that describe the chemistry of this type of situation are as follows:

Reaction #1 (Sulphide to Sulphate)

When natural sulphuritic material in the form of a sulphide (and usually in combination with iron) is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition:

(a) Assuming that the process takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of (water soluble) ferrous sulphate:

$$FeS_2 + 3\ O_2 \text{ ------> } FeSO_4 + SO_2$$

(b) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapour), then the direct formation of sulphuric acid and ferrous sulphate in equal parts results:

$$2\ FeS_2 + 2\ H_2O + 7\ O_2 \text{ ------> } 2\ FeSO_4 + 2\ H_2SO_4$$

In most mining environments (underground as well as in the tailings area), the above reaction is favoured.

Reaction #2 (Oxidation of Iron (Ferrous to Ferric))

Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state to form (water soluble) ferric sulphate:

$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \text{ ------> } 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Most evidence seems to indicate that a specific bacterium (T. ferrooxidans) is involved in the above reaction and is responsible for, at least, accelerating the oxidation of the ferrous iron to the ferric state.

Reaction #3 (Precipitation of Iron)

The ferric iron associated with the sulphate ion commonly combines with the hydroxyl $(OH)^-$ ion of water (HOH) to form ferric hydroxide. In an acid environment, ferric hydroxide is largely insoluble and accordingly precipitates:

$$Fe_2(SO_4)_3 + 6\ H_2O \text{ ------> } 2\ Fe(OH)_3 + 3\ H_2SO_4$$

IMPORTANT NOTE

The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion "backtriggers" the oxidation of further amounts of sulphuritic materials (iron sulphides, etc.) to the sulphate form thereby accelerating the acid-forming process:

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \text{ ------> } 3\ FeSO_4 + 2\ S^o$$

$$S^o + 3\ O + H_2O \text{ ------> } H_2SO_4$$

Sources and Characteristics of Acid Mine Drainage

At the present time, approximately fifty square miles of the Province of Ontario are covered by active and abandoned tailings areas. Many of these areas are pyritic in nature. The significance of this is that acid mine drainage is a cumulative problem because abandoned properties continue to produce 'acid' for decades. Therefore, as the number of abandoned sulphide operations increases, the acid load to the environment also increases.

In the past, two types of sulphide deposits have not been commercially recoverable in Ontario. One was the relatively low grade, large volume type of deposit and the other was the type of deposit that was characterized by complex fine-grained sulphide assemblages. In general, both of these types of deposits are now being successfully worked. The low grade, large volume type of deposit generates large volumes of tailings that may or may not contain significant quantities of iron sulphides. The complex sulphide-assemblage type of deposit is frequently associated with large quantities of the iron sulphide minerals which, as stated before, are rejected to tails as wastes. Many individual pyritic tailings areas in the Province cover hundreds of acres

and many new large ones are expected. One such tailings area in the Province will ultimately cover nearly four square miles and will have an inherent iron sulphide content in excess of 30 percent.

Tailings areas that are well known as acid producers in the Province of Ontario have iron sulphide contents ranging from 2.5 percent to 72 percent. It is suspected that acid mine drainage conditions will occur even when the iron sulphide content of a tailings mass is less than 2.5 percent.

Complex sulphide assemblages frequently require very fine grinding in order to liberate individual sulphide species. The individual species are recovered as separate concentrates by a process called differential flotation. Unfortunately, the iron sulphide minerals in the ore must also suffer the fine grinding procedure. As the grind becomes finer, the relative surface area of each sulphide particle increases. As the relative surface area of each sulphide particle increases, the probability of an acid mine drainage situation increases. Two years ago, a mill grind of 65 percent minus 200 mesh was common. Today, grinds finer than 300 mesh are becoming common.

The iron sulphides, pyrite, pyrrhotite and marcasite are not the only sulphides that are discharged

to a tailings area. There are over 125 naturally occurring inorganic sulphides and sulphosalts and many of these are well known 'ore' sulphides. Since mill efficiencies are seldom greater than 97 percent, limited quantities of these sulphides also gain access to a tailings area. The 'ore' sulphides are subject to chemical attack especially under the extreme conditions that are created by the oxidation of the iron sulphides.

Some metals, cobalt and nickel for example, can substitute for iron in the iron sulphide lattice. When the iron sulphide lattice breaks down, these metals also go into solution if the sulphide is in an aqueous environment.

Acid conditions are frequently generated in underground mining environments where oxygen-carrying water is permitted to come into contact with sulphide-bearing rock masses. This water must be removed from the mine and its disposal is a problem.

Typical acid mine drainage flows are characterized by a low pH, a high iron concentration, a high sulphate concentration and an abnormal heavy metals concentration. Manganese, copper, cobalt, zinc and nickel are all commonly found in acid mine drainage flows. The list of the possible anions and cations that can occur

in an acid mine drainage type effluent is almost endless.

Soluble iron compounds, which are an integral part of most acid mine drainage flows, tend to oxidize over a period of time. The resulting complexes or finely divided precipitates are various shades of yellow or red in colour. Amber stagnant pools of this type of waste and yellow-tinted seepage flows typify a mining camp that is, or has been, subject to acid mine drainage.

The development of an acid mine drainage situation at a mining property is probable if:

(a) the ore (including country rock) being milled contains iron sulphide minerals; and

(b) the ore (including country rock) does not naturally contain enough carbonate or similar material to effectively neutralize all the 'acid' that will result from the decomposition of the iron sulphides.

The probability of an acid mine drainage situation increases:

(a) with an increase in fineness of grind in a mill circuit. As the grind becomes finer, the total available surface area for reaction increases.

(b) with an increase in the number of permeable dams on the property or with an increase in the length of existing permeable dams on the property. Seepage flows

through the dams act as the transport medium for the soluble reaction products of sulphide decomposition. If the soluble reaction products are not removed, connecting pore spaces in the tailings mass become clogged with these substances and the acid mine drainage mechanisms are forced to slow down because of a lack of available oxygen, water and soluble ferric iron.

(c) with the return of untreated seepage from the bases of dams to the main tailings area. In acid mine drainage situations, untreated seepage contains quantities of dissolved ferric iron. This ferric iron can cause the oxidation of further amounts of iron sulphide should it come into contact with iron sulphide.

Chemical Treatment of Acid Mine Drainage

The treatment of acid mine drainage at the present time involves some form of neutralization. Neutralization is necessary to control pH and to precipitate soluble metallic species. In some instances, neutralization to a minimum pH of 8.5 is sufficient. In other instances, a minimum pH of 8.5 will still leave a few metals in solution. Accordingly, the pH must be increased until, if technically feasible, total precipitation is achieved. Where the pH is increased to a very high level (over 10) to achieve total precipitation

of the metals, adjustments will be required to reduce the pH to normal levels prior to discharge to a water-course.

Generally, five common neutralizing agents are available for use:

(1) ammonia
(2) sodium hydroxide
(3) sodium carbonate
(4) limestone
(5) lime

Because of its toxicity and nutrient properties, ammonia should never be used as an effluent neutralizing agent. Similarly, the use of ammonia and ammonium based compounds in a mill circuit should be avoided.

Sodium hydroxide and sodium carbonate are both acceptable as neutralizing agents but, because of their costs, do not find wide use. There is, however, an ecological advantage in using sodium carbonate as it will tend to offset any inorganic carbon deficiency in water that may result from discharges of the acid mine drainage type.

Lime and limestone are the most commonly used neutralizing agents. Lime finds the greatest use and, from a chemical standpoint, is the preferred reagent. Lime is generally available, has a high basicity and

the cost, while high, is less than all other neutralizing agents with the exception of limestone. Lime is a very reactive material with the neutralizing reaction going to completion within one hour. High pH's can be obtained and maintained with lime. In Ontario, where the removal of inherent heavy metal concentrations is required, this capability is very important.

The attractiveness of limestone as a neutralizing agent centres primarily on its low initial cost per unit weight and the fact that it presents almost no problems with regard to handling and storage. Its disadvantages, however, are numerous. The limestone neutralization reaction is slow and often requires from 24 to 48 hours to go to completion. The long detention time that is generally required after limestone addition to an acid effluent becomes significant when the land upon which the retention facilities are built is expensive or when numerous impoundment structures are required. Aeration may reduce the retention time to one comparable to lime. Neutralization with limestone tends to become inefficient above pH values of 4.0. pH's above 7.0 are obtained and maintained with some difficulty. Total utilization of the potential alkalinity of limestone can drop to approximately 31 percent. In contrast, the

utilization efficiency of lime is generally in excess of 97 percent. During the neutralization process, the limestone particles become coated with insoluble reaction products. If this coating is not continuously removed, the reaction is retarded. In any case, the limestone reaction seldom goes to completion and the resulting limestone sludge contains a residual alkalinity that is of questionable value. Limestone, under most circumstances, exhibits an inability to effect complete control of dissolved ferrous iron whereas lime handles this material with relative ease. In Ontario, where acid seepage flows frequently contain considerable concentrations of dissolved ferrous iron, this is an important factor. One dubious advantage of the limestone reaction is that it is not very sensitive quantitatively and therefore the accuracy with which limestone is fed into an effluent stream need not be controlled to the same degree as that required by lime.

Fixed beds of limestone are not recommended for neutralization of final effluents.

When acid mine drainage conditions prevail, iron is the principal metal found in solution. Depending on many factors, the iron will be either in the suspended or dissolved form and in the ferrous (Fe^{++}) or

the ferric (Fe^{+++}) state. In the pH range below 3.0, most of the ferrous and ferric iron will be in solution. In the pH range 3.0 to 8.0, the ferric iron should all be in a precipitate form and, while much of the ferrous iron will also be in a precipitate form, a significant portion of the ferrous iron will also be in solution. In the pH range above 8.0, essentially all iron species are insoluble and hence precipitate. In acid mine drainage circumstances, ferrous and ferric iron are generally associated with the sulphate radical. Ferric sulphate hydrolyzes in an aqueous environment to form an insoluble hydroxide plus sulphuric acid. The acid released can cause a pH depression. Ferrous iron in a stream will oxidize to the ferric form and then hydrolyze to form the hydroxide and sulphuric acid. Since ferrous iron exhibits a greater stability in acid and somewhat alkaline environments then does ferric iron, the ferrous ion has the potential ability to migrate much farther from a tailings area than does the ferric ion. However, as the distance between the ferrous ion and the tailings area increases, conditions for the survival of the species deteriorates and, ultimately, oxidation and hydrolysis takes place.

Several chemical agents which are indigenous

to mine drainage waters have been cited in the literature, in various circumstances, as displaying catalytic properties in the oxidation of ferrous iron. These include inorganic ligands, such as sulphate, which co-ordinate with iron (II) and iron (III); soluble metal ions such as copper (II), manganese (II), and aluminum (III): suspended material with large surface areas and high adsorptive capacities such as clay particles; and materials which accelerate the decomposition of peroxides in the presence of iron (II) such as charcoal.

Microbiological Aspects of Acid Mine Drainage

A topic that is frequently associated with the subject of acid mine drainage is microbiological leaching of sulphide minerals. Microbiological leaching involves the oxidation of the sulphide portion of various metallic sulphides with the subsequent release of the metal values into solution. Three names have been given to bacteria capable of oxidizing sulphide minerals:

(1) Thiobacillus ferrooxidans;
(2) Ferrobacillus ferrooxidans; and
(3) Thiobacillus sulfooxidans.

However, it has been shown that there is no justification for separating the bacteria into different genera and species and, as such, the name T. ferrooxidans has been suggested for the group.

Like many bacteria, T. ferrooxidans is ubiquitous, and its activities are manifested in leaching wherever a sulphide substrate, oxygen, carbon dioxide, water, certain essential nutrients and the correct pH make up a suitable environment.

T. ferrooxidans belongs to a somewhat select group of bacteria which are rather independent in temperament, and which probably existed on this earth long before those other microbial forms which are interdependent for many of their foods and conditions of life. In contrast to most bacteria, T. ferrooxidans uses atmospheric carbon dioxide as its sole source of the carbon necessary for the generation of cellular material. Rather than utilizing organic matter such as fats, carbohydrates or proteins as a source of energy, this organism cannot even tolerate their presence, and obtains its energy solely by the oxidation of inorganic materials such as ferrous iron or sulphur in the form of elemental sulphur or as metallic sulphides.

T. ferrooxidans has adapted itself to live and grow in the strongly acidic environment (pH 1.5 - 3.0) which results from the oxidation of sulphides, and in the presence of many heavy metals which are released into solution from minerals concurrent with the oxidation of

ferrous iron and sulphides. In order for T. ferrooxidans to function in the biological leaching of sulphides, the pH must be below 4 and preferably below 3. Apparently, the organism can oxidize sulphur at pH's as high as 5, but it will only occasionally oxidize sulphide at pH's above 3.5, and never above 4.0.

In attacking the sulphide moiety in crystalline or amorphous substances, the bacteria convert the sulphide to sulphate and, with the disruption of the solid matrix, the metal ions go into solution. These metals remain in solution as water-soluble sulphates initially, although iron may be subsequently precipitated as the insoluble hydroxide or basic sulphate. The hydrolysis of the ferric sulphate produces sulphuric acid along with either the ferric hydroxide or basic ferric sulphate. The sulphuric acid modifies the pH in the microenvironment immediately surrounding the bacteria. If there is no external disruption, the pH frequently tends to stabilize near pH 2 due to the resolubilization of ferric hydroxide. If there is excess pyrite or pyrrhotite present, it will go lower; pH values as low as 0.9 having been attained. pH values below 1.2 have a definite detrimental effect on the bacteria, interfering with their activity and resulting in the production of

elongated cells.

Although T. ferrooxidans survive in conditions that are highly toxic to most other forms of life, it still must have oxygen to live. Every pound of sulphur (either as native sulphur or as sulphide) requires two pounds of oxygen for complete conversion to sulphate. Similarly, the bacteria require 0.14 pounds of oxygen for every pound of iron converted from the ferrous to the ferric form.

Phosphate and ammonia appear to be the most critical nutrients with regard to the nutrient requirement of T. ferrooxidans.

Temperature is another factor which can influence biological leaching. The optimum temperature for biological leaching has been found to be 35° C. The bacteria are inhibited at temperatures of 40° C and above. When no other factors have become rate controlling, the rate of leaching decreases as the temperature decreases; as yet, however, no minimum temperature has been established. Leaching is known to occur slowly at 3°C to 6°C.

Substrates Oxidized by Thiobacillus Ferrooxidans

Substrate	End Product
Ferrous Iron Fe^{++}	Fe^{+++}
Trithionate $S_3O_6^{=}$	$SO_4^{=}$

Substrate		End Product
Tetrathionate	$S_4O_6^=$	$SO_4^=$
Thiosulphate	$S_2O_3^=$	$SO_4^=$
Sulphur	S^o	$SO_4^=$
Sulphide	$S^=$	$SO_4^=$

Metallic Sulphides Known to be Oxidized by Thiobacillus Ferrooxidans

Arsenopyrite - $Fe_2AS_2S_2$

Bornite - Cu_5FeS_4

Bravoite - $(Ni, Fe)S_2$

Chalcocite - Cu_2S

Chalcopyrite - $CuFeS_2$

Cobaltite - CoAsS

Covellite - CuS

Enargite - $Cu_3(As, Sb)S_4$

Marcasite - FeS_2

Marmatite - (Zn, Fe)S

Millerite - NiS

Molybdenite - MoS_2

Orpiment - As_2S_3

Pyrite - FeS_2

Pyrrhotite - Fe_7S_8

Sphalerite - ZnS

Stannite - Cu_2FeSnS_4

Tetrahedrite - $Cu_8Sb_2S_7$

Violarite - $(Ni, Fe)_3S_4$

The Reaction of Non-Sulphide Minerals Under Acid Mine Drainage Conditions

The decomposition of sulphides in a tailings area frequently creates chemical conditions that adversely affect the stability of many of the non-sulphide mineral species that are present. Although these non-sulphide minerals are, in general, characterized by their relative stability in a natural environment, they do break down

very slowly and release anions and cations that help to make up natural background concentrations. In a tailings basin, the enormous overall surface area of the tailings mass itself is such that the slow breakdown of the various non-sulphide minerals becomes significant since the soluble reaction products frequently end up in a concentrated form in the seepage or decant overflow from the area. A few grams of tailings taken from almost any disposal area will contain at least traces of most of the elements known to man. It is for this reason that strict attention must be paid to the type and reactivity of all minerals that occur in or are associated with an orebody. As an example, consider the rocks known as granite and diabase. Both occur commonly in and around ore bodies. Granite is essentially composed of feldspar and quartz. Minor constituents may include muscovite, biotite, hornblende and, rarely pyroxene. Diabase is essentially a mixture of feldspar and pyroxene. Table I, presented at the end of this paper, indicates the relative amounts of the various elements that could be released if total decomposition of granite and diabase took place.

If complete treatment is not provided, an exposed tailings area, particularly if it is subject to

an acid mine drainage situation, will permit the escape of many unwanted materials into our natural aqueous environment.

Revegetation

The revegetation of abandoned mine tailings in the Province of Ontario is now mandatory under the provisions of The Mining Act.

The presence of a well-developed cover of vegetation reduces the effects of acid mine drainage by regulating the effect of natural precipitation and thereby reducing the volume of acid seepage flows. However, a vegetative cover does not completely eliminate seepage flows and, as a result, some form of chemical treatment of waste flows is generally still required.

The revegetation of tailings areas that contain quantities of the iron sulphide minerals is difficult and expensive. The main problem is the acid condition that is generated by the slow decomposition of the sulphide minerals. The 'acid' that is produced must be neutralized before any seeding of the area is attempted. In addition, a large reserve of residual alkalinity must be provided so that 'alkalinity' is available on a continuous basis. The iron sulphides spontaneously produce acid and if this is not neutralized as it is formed, a

'kill' of any established vegetation could take place. However, it is probable that, once a cover of vegetation has been established, naturally introduced acid tolerant species of vegetation will take over.

The initial neutralization of the upper few inches of an acid tailings area prior to seeding can be accomplished with powdered lime or finely-divided limestone or a mixture of both. The residual alkalinity should be attained and maintained with a graded limestone product.

Limestone tends to be quite expensive in the mining districts of Ontario simply because the mining camps are frequently to be found considerable distances from the limestone producing centres in southern Ontario.

It should be emphasized that the limestone required for maintaining alkalinity in the upper layers of a pyritic tailings area need not be pure. Quite often the limestone can be found in sedimentary strata, sedimentary outliers, or metamorphic equivalents of carbonate sediments within a reasonable trucking distance of the mining operations. Gravel deposits that have been derived by glaciation from the aforementioned often contain significant quantities of carbonate pebbles. Pit-run or screened gravel is much cheaper than crushed limestone.

Water Recirculation

When mining activities began in the Province over one hundred years ago, there was little apparent need for strict water conservation. Today, the awareness and demands of a rapidly increasing population have changed the picture dramatically. Even the most remote mining operation is now subject to stringent environmental controls.

Wastewater re-use is a very effective way to lessen the impact of a mining operation on its immediate environment. By reducing the total volume of waste discharged from any particular operation, water recycle permits several mining companies to exist with some degree of environmental compatibility on a single lake, single watercourse, or single watershed. This sharing of a restricted area is the rule rather than the exception in the mining industry.

The most effective way to minimize an overall acid mine drainage problem during the years of conventional mine-mill operations is to reduce the total volume of effluent that leaves the property. The most convenient way to reduce the total volume of effluent leaving the property is to set up the mine-mill complex on the basis of total or at least partial water recircula-

tion.

Total recirculation in many sections of the mining industry is not easy to attain. Flotation circuits, for instance, are noted for their sensitivity. Even the simple re-use of underground (or open pit) mine water in the grinding bay of a mill that employs normal froth flotation circuits can theoretically cause problems if the water contains significant quantities of organic materials such as oil. The occurrence of trace quantities of oily materials in underground mine water as a result of mining operations is not only possible but is probable. The recirculation of a tailings area decant involves even more. The tailings area decant can and often does contain residual quantities of the more persistent milling reagents. If the decant is indiscriminantly recirculated to the mill, the mill operator can lose partial control of the flotation process with the result that valuable concentrate is lost. Similarly, abnormal quantities of soluble and suspended materials that are reintroduced into a mine-mill circuit have a potential ability to adversely affect basic operations such as ion exchange, thickening, filtration, precipitation and pH control. When all of this is added to the fact that most underground mines naturally "make"

more water than can be used in underground mining operations and the fact that natural precipitation on a tailings area frequently creates a significant oversupply of water as far as recirculation from a tailings area decant to a mill is concerned, it becomes obvious that total recycle is often impossible to achieve. However, partial recycle is possible in nearly every case.

All new mine-mill complexes coming into production in the Province of Ontario are currently being requested to set up their mine-mill operations on the basis of maximum possible water re-use. In existing problem areas, mining operations are also being requested to effect maximum possible water re-use.

Summary

Acid mine drainage is one of the greatest single environmental problems facing the sulphide mining industry in Ontario today. Quick and intelligent action is required. A parallel can be drawn to the mining districts of the eastern United States where neglect of the problem of acid mine drainage has led to the impairment of over 10,000 miles of previously unaffected watercourses.

The industrial wastes program in Ontario contains the ingredients necessary to adequately control

the major aspects of any acid mine drainage problem. However, complete control will be won only through the concerted efforts of government agencies coupled with the absolute cooperation of the industries involved.

TABLE I

The Average Amounts of the Elements in Crustal Rocks in Parts Per Million

(omitting the rare gases and the short-lived radioactive elements)

Atomic Number	Element	Crustal Average	Granite	Diabase
1	H	1,400	400	600
3	Li	20	24	12
4	Be	2.8	3	0.8
5	B	10	2	17
6	C	200	200	100
7	N	20	8	14
8	O	466,000	485,000	449,000
9	F	625	700	250
11	Na	28,300	24,600	15,400
12	Mg	20,900	2,400	39,900
13	Al	81,300	74,300	78,600
14	Si	277,200	339,600	246,100
15	P	1,050	390	650
16	S	260	175	135
17	Cl	130	50	
19	K	25,900	45,100	5,300
20	Ca	36,300	9,900	78,300
21	Sc	22	3	34
22	Ti	4,400	1,500	6,400
23	V	135	16	240
24	Cr	100	22	120
25	Mn	950	230	1,320
26	Fe	50,000	13,700	77,600
27	Co	25	2.4	50

Atomic Number	Element	Crustal Average	Granite	Diabase
28	Ni	75	2	78
29	Cu	55	13	110
30	Zn	70	45	82
31	Ga	15	18	16
32	Ge	1.5	1.0	1.6
33	As	1.8	0.8	2.2
34	Se	0.05		
35	Br	2.5	0.5	0.5
37	Rb	90	220	22
38	Sr	375	250	180
39	Y	33	13	25
40	Zr	165	210	100
41	Nb	20	20	10
42	Mo	1.5	7	0.05
44	Ru	0.01		
45	Rh	0.005		
46	Pd	0.01	0.01	0.02
47	Ag	0.07	0.04	0.06
48	Cd	0.2	0.06	0.3
49	In	0.1	0.03	0.08
50	Sn	2	4	3
51	Sb	0.2	0.4	1.1
52	Te	0.01		
53	I	0.5		
55	Cs	3	1.5	1.1
56	Ba	425	1,220	180
57	La	30	120	30
58	Ce	60	230	30
59	Pr	8.2	20	2

Atomic Number	Element	Crustal Average	Granite	Diabase
60	Nd	28	55	15
62	Sm	6.0	11	5
63	Eu	1.2	1.0	1.1
64	Gd	5.4	5	4
65	Tb	0.9	1.1	0.6
66	Dy	3.0	2	4
67	Ho	1.2	0.5	1.3
68	Er	2.8	2	3
69	Tm	0.5	0.2	0.3
70	Yb	3.4	1	3
71	Lu	0.5	0.1	0.3
72	Hf	3	5.2	1.5
73	Ta	2	1.6	0.7
74	W	1.5	0.4	0.45
75	Re	0.001	0.0006	0.0004
76	Os	0.005	0.0001	0.0004
77	Ir	0.001	0.006	
78	Pt	0.01	0.008	0.009
79	Au	0.004	0.002	0.005
80	Hg	0.08	0.2	0.2
81	Tl	0.5	1.3	0.13
82	Pb	13	49	8
83	Bi	0.2	0.1	0.2
90	Th	7.2	52	2.4
92	U	1.8	3.7	0.52

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RECOMMENDED WASTE CONTROL PROCEDURES FOR NEW MINING OPERATIONS IN ONTARIO

by

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RECOMMENDED WASTE CONTROL PROCEDURES FOR NEW MINING OPERATIONS IN ONTARIO

Ontario, a prime natural store-house for a significant percentage of man's fresh water supply, is one of the richest mining districts in the world. Covering over 344,000 square miles, the ancient and crumpled surface of this Canadian province is dotted with 250,000 fresh water lakes and is laced with uncounted thousands of fresh water rivers and streams.

It is in Ontario that the Canadian mining industry has excelled in its efforts to face the environmental problems of today. The attitude of the mining industry in Ontario has been admirably expressed by the Ontario Mining Association as follows: "as inhabitants of the North, we (the mining industry) are concerned with maintianing the co-partnership of nature and industry and, with Government, take pride in our North and its many attractions".

Whenever a new orebody is located in Ontario, a foregone conclusion is that the ensuing mine-mill complex will be on or near a watercourse. Natural conditions of geology and geography invariably combine to make this supposition true. A problem arises, however,

when one realizes that the fresh waters of northern Ontario are such that even minor discharges of foreign material to these waters have the potential ability to adversely affect quality and the life forms indigenous to these waters.

With the above in mind, the following comments are presented which concern water quality and wastewater treatment in locations where new mine-mill operations are to come into existence:

(A) DEVELOPMENT WATER, DEWATERING OPERATIONS

Many "new" mining properties are, in reality, properties which have already been worked in the past. If a mining company wishes to re-estimate the mineral potential of any specific property that includes abandoned underground workings, one of the first steps taken will generally be the dewatering of the flooded workings. The total volume of the water discharged from the workings depends almost entirely on the total volume of workings to be dewatered. The chemical characteristics of the discharge depend heavily on the chemical composition and 'reactivity' of the ore and/or waste rock penetrated by the workings, the surface area of the workings, and the length of time that the water has been in contact with the ore or

waste rock. As a result, the water pumped from abandoned workings will vary in nature from 'highly contaminated' to 'uncontaminated'.

In general, water being discharged from abandoned mine workings to a watercourse should exhibit a pH in the neighborhood of 7 and should not carry individual metals in concentrations greater than one part per million. Sodium, potassium, calcium and magnesium are the exceptions to this rule as these four metals do not significantly affect water quality or aquatic biota in the concentrations that are normally found in mine-mill discharges.

Some of the metals and other elements to check for in water from abandoned mine workings are as follows:

arsenic	copper	nickel
cadmium	iron	phosphorus
chromium	lead	vanadium
cobalt	manganese	zinc

Once an abandoned mine (open pit or underground) has been dewatered, development work (if justified) commences. In some cases, this work may consist only of sampling the exposed rock faces for mineral values. In other cases, an underground diamond drilling program may be carried out. In advanced stages, drifting, crosscutting and stope preparation are necessary. Under the above circumstances, the principal adverse characte-

ristic of the resulting wastewater discharges tends to be an undesirable suspended solids concentration. Significant metal concentrations may be associated with the suspended solids. If the wastewater from development work is to be discharged to a lake or stream in Ontario, the wastewater must not contain more than 15 parts per million of suspended solids.

(B) SOURCE OF WATER CONTAMINANTS

Contaminants that find their way into mine-mill waters have two basic and very important sources. These sources are:

(i) the ore (and country rock); and

(ii) the chemical reagents that are used in the mill and in the mine.

Most Ontario ores contain 'reactive' minerals (example, pyrite) which break down to form water soluble salts. These salts can be carried away by any water that happens to be present. Hence, underground mine water is frequently contaminated with these salts as are the various flows from tailings areas. This entire subject is explored in detail in a report entitled "The Problem of Acid Mine Drainage in the Province of Ontario", which is available free-of-charge from the Ontario Ministry of the Environment.

One of the easiest ways to determine what metals will appear in various mine-mill wastes (tailings area seepage, underground mine water, etc.) before a new mine-mill complex is in operation is to completely analyze small individual samples of all the minerals that commonly occur in the ore at the property in question. Particular attention should be paid to the iron sulphide minerals (pyrite, marcasite and pyrrhotite). Each mineral specimen (for example sphalerite, galena, chalcopyrite and pyrite) at the property should be subjected to, at least, the following tests:

arsenic	lead	tin
cadmium	lithium	titanium
chromium	manganese	vanadium
cobalt	mercury	zinc
copper	molybdenum	
iron	nickel	

If the results are recorded in "parts per million", one will be amazed at the overall composition of even such a simple mineral as pyrite. When pyrite or similar reactive minerals break down, they release all of their components. Some of these components (such as copper, cobalt, zinc and manganese) are invariably water soluble.

The most obvious source of water contaminants at an active mine-mill operation is, of course, the

chemical reagents (including explosives) that find everyday use in the mine and in the mill. Again, this subject is covered in detail in a recently released report by the Ontario Ministry of the Environment. Available free-of-charge, the report is entitled "Use, Characteristics and Toxicity of Mine-Mill Reagents in Ontario". Although the report is very specific, some general conclusions have been drawn. These are as follows:

(i) Mine-mill reagents vary in toxicity. Some are highly toxic while others, considering the circumstances of use, are relatively non-toxic. Some are persistent and hence will escape from a tailings area to downstream waters. Others are unstable and will break down in a tailings area. When reagents are being chosen for use in a mining operation, the least toxic compounds available should be chosen wherever possible. Included in the definition of 'least' toxic compounds are those toxic compounds that break down rapidly (into innocuous substances) in a waste stream or those toxic substances which can be removed easily from a waste stream using accepted

waste treatment technology.

(ii) The use of mine-mill reagents that are persistent (that is, reagents that do not break down easily in a natural environment) should be avoided if possible.

(iii) The use of mine-mill reagents having known or suspected nutrient properties should be avoided if possible.

(iv) When choosing a reagent for use in a mine-mill circuit or process, the total effect of that particular reagent on the receiving watercourse should always be considered. Reagent characteristics to investigate, for instance, would generally include chemical oxygen demand, biochemical oxygen demand, biodegradability, effects on local aquatic life (plant and animal) and effects on the total dissolved solids concentration and hardness of the receiving stream.

(v) The use of mine-mill reagents that consist of or contain water-soluble salts of metals that are known to exhibit undesirable environmental effects should be avoided if possible.

(C) WASTEWATER RECYCLE

In the mining industry and particularly for new mines, wastewater recycle should be actively explored for it:

(i) significantly reduces the total volume of fresh water that is required daily to sustain processing operations.

(ii) significantly reduces the total volume of wastewater that is discharged to the environment.

(iii) reduces waste loadings from a property since reagent additions in the mill will, in all probability, be reduced. Also, precipitation, coagulation and settling effects in the tailings area, on a recycle basis, will tend to reduce overall waste loadings of many contaminants.

(iv) reduces the required size of all waste treatment units due to the lower volume of all waste flows. Also, recycle permits the installation, if necessary, of very efficient and specific waste treatment units that are generally not available in sizes that are able to handle very large volume waste flows.

The recirculation of mine-mill wastewaters is

now becoming more commonplace in the Province of Ontario. Re-use of treated mine-mill wastewaters is a standard recommendation of the Ontario Ministry of the Environment. A tailings area should be designed with wastewater recirculation in mind. In essence, this means that a tailings area decant should be directed to a secondary area where chemical waste treatment (if required) can take place. When this has been accomplished, the clarified waste can be re-used for process purposes.

It is important to note that it is not wise to recycle wastewater (especially at a small mining operation) from the primary settling pond itself. The reason for this is that the presence of rock slimes (very finely divided rock particles) in the recycled water can seriously inhibit mill processes such as differential flotation and ion exchange with resultant losses in metallurgical efficiency. Recycle should only be attempted from the secondary area and, if necessary, aeration equipment can be installed in the secondary area to enhance the breakdown or removal of residual quantities of undesirable reagents.

Environmental control is only one of the many problems that the mining industry must face today. Present technology, however, is such that many environ-

mental problems have been defined but few have been completely solved. It is therefore necessary for the public, the government and the industry to work together to achieve satisfactory control of pollution problems arising from mining operations.

MINING EFFLUENTS AND THEIR CONTROL IN THE PROVINCE OF ONTARIO CANADA

by

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MINING EFFLUENTS AND THEIR CONTROL IN THE PROVINCE OF ONTARIO CANADA

INTRODUCTION

Ontario, one of the richest mining districts in the world, is a natural storehouse for much of the earth's fresh water supply. Covering over 344,000 square miles, the surface of this Canadian Province is dotted with 250,000 fresh water lakes and is laced with uncounted thousands of fresh water rivers and streams.

The southern portion of the Province, for the most part, is flat or lazily rolling farmland. This is where most of the people in Ontario live. Although it is not a major mining area, southern Ontario does possess important deposits of salt, oil, gas and gypsum. Most of these deposits are being actively worked.

Toronto, the capital city of Ontario, lies deep in the southern region. Here the climate is mild and the winters are short. The total annual precipitation consists of 27 inches of rain and 65 inches of snow. Most of the major mining companies that do business in Canada have made Toronto their Canadian headquarters. There are two reasons for this. The first, of course, is money. Toronto is the gathering place of many well-known financial institutions. The second is access. Toronto lies within a few hundred miles of some of the most spectacular mining

enterprises that exist in the world.

In Ontario, most of our important mines are located in Precambrian rock that forms part of the internationally famous Canadian Shield. The climate in the shield region of Ontario is much more severe than that in the southern region. The annual precipitation in the shield region consists of approximately 31 inches of rain and 112 inches of snow. Although summer temperatures in excess of 90^{o} F are not uncommon, winter temperatures below minus 40^{o} F are frequent.

Some of the shield mining area in Ontario could be classified as semi-mountainous but, in general, the local relief although wildly varied, is low and the skyline monotonously even. Dense evergreen forests cover most sections. Swamps are abundant. The cold and snow hamper mining exploration and development to some extent during the winter months and biting insects makes outdoor work unpleasant during the summer months.

At the present time, there are over 100 significant active mining operations in Ontario. Most are working metal deposits. A few are working non-metal deposits. Some of the materials being recovered on a commercial basis are copper, lead, zinc, iron, uranium, gold, silver, platinum, cobalt, nickel, palladium, iridium, rhodium, ruthenium, asbestos, talc, and nepheline syenite. Massive production of substances such as cadmium, tin, titanium, the rare earths, coal, phosphates and a host of others have also been carried out or will be carried out

in the future.

When compared to mining operations in other countries, the mines in Ontario are neither large nor small. For example, the average plant at an iron property in Ontario is presently handling between 10,000 and 15,000 tons of ore per day. The uranium plants are handling, on a reduced basis, approximately 4,500 tons per day. The gold plants are handling an average of 700 tons per day and so forth. Many Ontario copper-nickel mines produce ore in excess of 5,000 tons per day. This ore is subsequently treated in mills that are capable of handling up to 35,000 tons per day. Many isolated mine-mill complexes exist throughout the Province. These operations commonly treat between 500 and 3,500 tons of ore per day.

Obviously, on a tonnage basis, most mines in Ontario are insignificant when compared to such giants as Bougainville Copper in the Pacific where a 200,000 ton per day open pit feeds a 90,000 ton per day concentrator. Some of the porphyry copper plants in the United States are also quite large. For instance, the Magma Copper Company operates a 60,000 ton per day copper flotation mill at San Manuel near Tucson, Arizona. In the same area, Pima Mining Company generates 53,550 tons per day of tailings. The thing to remember however is that, as far as profitable mining is concerned, average ore grades in Ontario are quite good and are far superior to the ore grades encountered in the porphyry-type deposits. Consider, for example, the largest copper-lead-zinc mine in

the Province. Here, a 38,000 ton per day (ore plus waste) mining operation produces enough feed to keep a 10,000 ton per day mill in constant operation. The mill feed contains approximately 2% copper, 1% lead, 10% zinc and contains 5.5 ounces of silver per ton.

Mineral production has increased steadily in Ontario. For example, in 1945 mineral production in Ontario was valued at $217,000,000. In 1971, in spite of adverse market conditions and a score of other negative factors, mineral production was valued at 1.6 billion dollars.

Without a doubt, it can be stated that within the boundaries of the Province of Ontario there exists a dynamic and highly diversified mining industry. The mills in Ontario range from small tar-papered shacks that house only the crudest of mineral dressing equipment to impressive layouts that whisper with the sophistication of almost complete automation. The mines themselves present a similar story. The smallest open pits (which are not even listed as mines) exist in their thousands. Generally owned or operated by one or two individuals, these "diggings" are seasonally worked for rare radioactive minerals, garnets, agates, zircon, beryl, corundum, sodalite, labradorite, amazonite and obscure substances and minerals that most of us have never heard of. On the other hand, some of the open pits that are being actively worked in the Province can be numbered among the largest man-made excavations in the world. The underground mines are no different. We have small mines that plunge to such awesome depths

as 50 feet and end as suddenly as did the financial resources of the operator and we have operations that work well below the 5000 foot mark and give hundreds of men employment.

Given all of the foregoing circumstances, it is not surprising that the mining industry in Ontario and the Government of Ontario have had to face a bewildering variety of mine-mill waste treatment problems. In nearly all cases, however, these problems have been adequately solved.

MINE-MILL WASTE TREATMENT

In Ontario, a mining operation will give rise to two PRIMARY liquid EFFLUENTS

(A) The mill slurry

(B) The mine water

(A) The Mill Slurry

In Ontario, any mill slurry produced by a mine-mill operation must be directed to an engineered impoundment area. A common size for these tailings areas in the Province is from 100 to 300 acres. Formal tailings areas that cover less than five acres do exist in Ontario as does a major tailings area that covers 1,200 acres. Tailings dams in Ontario are commonly less than 50 feet in height although dams in excess of this height are known in nearly all of the mining camps.

In Ontario, even though they are extremely abundant, a lake is not regarded as an acceptable tailings disposal site. In the early days of mining, lakes often fell prey to this fate. At

the present time, however, a lake will be assigned for tailings disposal only with the greatest possible reluctance on the part of the government.

In the early days of mining in Ontario there were no formal tailings areas and, as such, no tailings dams. Tailings produced at a mill were simply directed away from the mine-mill area and were left to find their own resting place on the landscape. With the introduction of the concept of suspended solids pollution, the tailings dam was born. Initially the sole function of a tailings dam was to stop the migration of abnormal amounts of suspended solids from the tailings area into adjacent watercourses. Indeed, this is still a major function of a tailings dam. In Ontario, for instance, an effluent from a tailings area may not contain more than 15 parts per million of suspended solids. In the past, in Ontario, tailings dams were designed in such a manner that water held in a tailings area could freely percolate through the tailings dams and could then emerge at the bases of the dams as seepage. Unfortunately it was found that, in many cases, this seepage was highly contaminated and required expensive chemical treatment. As a consequence, the trend in Ontario today is to construct tailings dams that are essentially impermeable. This has been done in various locations in Ontario and has been accomplished with the help of clay dam cores, concrete dam cores, synthetic rubber linings, and so on.

The materials of tailings dam construction in Ontario

vary widely. Glacial drift, local clays, mine waste rock and classified mill tails are all used depending on the availability of each and on the economics of the situation. All have their advantages and all have their disadvantages. However, experience gained in Ontario has shown that, if possible, the use of classified mill tails for tailings dam construction should be avoided. Dams composed of mill tails are highly susceptible to wind and water erosion. Minor failures are frequent and major failures tend to be spectacular.

In general, tailings areas should always be designed to minimize environmental effects due to problems such as acid or alkaline mine drainage. Some points to consider are as follows:

(a) A tailings area should be located as high in a watershed as possible. In other words, a tailings area should intercept as little uncontaminated runoff as possible.

(b) A tailings area should not be located in an existing lake basin or in a very wet swampy area. In fact, a tailings mass or even a waste rock mass should not cover any significant continuously-running source of uncontaminated water. If such a source is covered with reactive tailings or waste-rock, the uncontaminated water will become contaminated and, as such, the volume of water that should be treated will have increased unnecessarily.

(c) Whenever and wherever possible, tailings dams should be impermeable. Impermeable dams do not give rise to visible

contaminated seepage flows.

(d) All seepage flows from the bases of permeable dams should be collected for treatment. As such, a trench which acts to intercept surface seepage flows should be constructed parallel to and a short distance from the downstream side of all permeable dams on the property. The waste collected by each trench should be directed to a central treatment facility. Sub-surface seepage flows from a tailings area may, in some instances, be the cause of detectable environmental problems. In such cases, appropriate action should be taken.

(e) Some adverse environmental situations, such as the problem of acid mine drainage, do not reach a peak in Ontario until after a mining property has been abandoned. In Ontario, waste treatment must continue as long as a problem exists. For this reason, many abandoned mining operations in the Province are equipped with complete automatic waste treatment facilities that function summer and winter. Since, in many cases, waste treatment must continue long after a property has been abandoned, it is wise to avoid mechanical pumping facilities whenever and wherever possible. A gravity flow which, on occasion, is more expensive to install at the outset, will be more economical in the long run.

(f) A tailings area decant should always be located as close as possible to the mill. Since waste treatment facilities will generally be located at or near a tailings area decant,

a decant treatment facility close to the mill will:

(i) permit shorter hydro lines to the site.

(ii) permit shorter access roads to the site and will hence reduce road construction and maintenance costs.

(iii) permit shorter wastewater recycle etc., lines from the site to the mill. Subsequent savings will be realized in pumping costs, insulation costs and so forth.

(iv) in some cases permit waste treatment reagent storage tanks, mixing tanks etc., to be located in the mill itself. Under these circumstances, waste treatment reagents could be pumped directly to the treatment area thus eliminating the expense of a heated and automatically controlled waste treatment building at the treatment site itself.

(g) Generally speaking, a tailings area itself should not be regarded as a chemical waste treatment facility. Instead, the tailings area decant (plus all tailings area seepage) should be directed to a chemical waste treatment facility. In a few cases, the chemical waste treatment facility required may, of necessity, be somewhat elaborate. In most cases, however, the facility might consist of nothing more than one or two formal ponds of various sizes that are operated in series. In exceptional cases, more than two ponds could be required. The total industrial effluent (after solids removal in the tailings area) would enter the first pond. Any required

chemical additions would be made at the tailings area decant. The first pond, fed by the tailings area decant would act as a settling basin and would retain any precipitate that was initiated by the chemical additions to the decant overflow. A second pond might act as an alternate pond to permit, when required, the cleaning (sludge removal) of the original first pond. On the other hand, the second pond, fed by the first pond, might be used as a source of recycle water or as a final effluent polishing pond (for final pH adjustment, etc.).

Note: It is very difficult to control the pH of a tailings area decant by neutralizing reagent additions in the mill itself. The very size of an average tailings area indicates the lack of response that may be expected at the decant point as a result of varying the quantity of neutralizing reagent additions in the mill. Also, the extremely high suspended solids content of most mill discharges to a tailings area must, by processes such as adsorption, reduce the effectiveness of any such neutralizing reagent additions. The required final pH range at the decant may be acquired by greatly over-neutralizing the waste stream in the mill but this is an expensive process and it tends to unduly increase the concentration of total dissolved solids in the final effluent from the property. pH control for waste treatment purposes should always be carried out at the decant overflow. In this way, reagent additions (and reagent addition costs) are minimized. Increases in the concentration of total dissolved solids in the final effluent are also kept to a minimum.

(h) Wherever and whenever possible, tailings dams and related structures should be completed to their projected final height before milling commences at any specific property. All such structures should be immediately revegetated.

(i) Wherever and whenever possible, the revegetation of the

surface of a tailings area should take place as soon as an area or a portion of an area is abandoned.

(j) The design of a tailings area, especially a tailings area that is to be incorporated into a wastewater recycle scheme, should not be finalized until the following factors have been taken into consideration:

(i) Many important mine-mill reagents are organic compounds. Under certain conditions, most of these compounds will exhibit a degree of biodegradability or chemical instability.

(ii) Residual concentrations of mine-mill reagents have been identified in the effluents from mining operations that work sulphide ores. Xanthate residuals of 0.2 to 1.2 mg/litre and dithiophosphate residuals in the range of 0.3 to 2.7 mg/litre have been noted.

(iii) In general, the constituents of frothers are volatile substances. Accordingly, a substantial quantity of the frothers added in flotation operations is volatilized so that re-use of flotation tailing waters does not necessarily reduce proportionately the requirement for frothers. Unwanted quantities of a particular frother appearing in a recycle stream (from tailings area, etc.) can probably be reduced or eliminated by:

- increasing the retention time of the frother

containing wastes before recycle to the mill; or

- applying a degree of mechanical aeration etc. to the frother-containing waste; or
- selecting another frother with superior breakdown properties for use in the mill.

If the breakdown properties of a particular frother are known, then the actual waste retention time in the tailings area serving the operation can probably be increased to effect substantially a complete breakdown (or loss) of the frother or decreased to prevent frother loss or breakdown (if this is desired).

(iv) The xanthates are among the most toxic reagents that find common use in a sulphide mill circuit. They are, however, quite unstable in aqueous solution and break down into relatively innocuous substances. At temperatures above 30^{o} C and at low (xanthate) concentrations (such as found in a tailings decant), and exposure to acidic conditions, decomposition of xanthates is extremely rapid. Therefore, it appears that residual xanathate concentrations can be reduced by increasing waste retention times and by decreasing solution pH values.

(v) The recirculation of mine-mill wastewaters is now becoming commonplace in the Province of Ontario. Water re-use is a standard recommendation of the

Ontario Ministry of the Environment. Therefore, a tailings area in Ontario should be designed with wastewater recirculation in mind. In essence, this means that the tailings area decant should be directed to a secondary (or downstream) area where chemical waste treatment and final solids removal can take place. When this has been accomplished, the clarified waste can be used for recycle purposes.

It is important to note that it is not wise to recycle wastewater (especially at a small mining operation) from the decant pond itself. The reason for this is that the presence of rock slimes (very finely divided rock particles) can seriously inhibit mill processes such as differential flotation and ion exchange with resultant losses in metallurgical efficiency. If necessary, aerators, etc., can be installed in the secondary area in order to enhance the breakdown or removal of residual quantities of undesirable reagents.

One point that has not been mentioned is that Ontario is an area of very low seismic activity. As such, there are no regulations that limit the height of a tailings dam. However, before a tailings area can be constructed in the Province, the company involved must submit detailed engineering drawings and soil reports etc. to the government for approval. If the works

are rejected, they must be redesigned. In its approval procedure, the government uses a relatively simple form that was specially designed for the Ontario mining industry. This form has been primarily responsible for upgrading the quality of the approval submissions from the mining industry and, working in reverse, has increased the government's appreciation of many of the technical mine waste treatment problems that face the industry.

It is interesting to note that, today, major tailings dam failures are very rare in Ontario. Most minor tailings area failures and, indeed, most major tailings area failures in the Province can be or have been attributed to failures of decant structures rather than to failures of tailings dams. In Ontario, most tailings area decant structure failures occur during the harsh winter months and during the days of spring break-up. It is during these times that massive blocks of ice floating in the decant pond can smash against the structures and thick sheets of ice can exert enormous pressures on the structures. Even so, failures are not common. During one recent winter, for instance, only three minor decant failures were recorded even though well over one hundred decant structures were operating all through that particular winter. It is also interesting to note that, in Ontario, many different materials are used in the construction of decant facilities. Ranging from simple squared wooden timbers to specially formulated and treated reinforced concrete, the structures are generally durable and provide an interesting

showcase of mine engineering technology. In fact, the absolute diversity of the mining industry in Ontario provides, to all those who are interested, a fascinating study of mining and mine waste treatment methods.

(B) The Mine Water

Mine water is another important PRIMARY EFFLUENT that is generated by the Ontario mining industry.

In Ontario, active open pit operations have not generally given rise to serious water pollution problems. Most active open pits remain relatively dry. The chemical characteristics of any water pumped from an active pit depends on

(a) the composition of the ore

(b) the surface area of ore available for chemical attack.

(c) the residence time of the water in the pit.

In most cases, water pumped from an active open pit operation is contaminated.

Natural precipitation and ground water flows will usually cause an abandoned open pit to fill or partially fill with water. Only rarely does a visible overflow take place. If the open pit operation resulted in the removal of all original ore, the water filling the pit may be uncontaminated. However, in most cases, the wall rock at least contains disseminated sulphides etc., and, as such, the pit water, over a period of years, can become highly contaminated.

It is not unusual for conventional underground operations to follow open pit operations at any particular property. When the property is completely abandoned, the workings may connect.

Water gains access to active underground mine workings in two ways; as downward percolating ground water and as water that is deliberately pumped into the workings by the company for process use.

As a result of faulting, etc., coupled on occasion with diverse solution effects, very sophisticated natural drainage networks can be set up within a particular mineral deposit. Faults, joints, torsion cracks, old drill holes etc., frequently directly or indirectly connect the mine workings with the surface and thus allow considerable water to flow into the workings. The network can be so efficient, in fact, that a company mining the deposit has to rely heavily on pumps to keep the workings dry. The volume of water that will gain access to a new mine working in Ontario cannot be predicted. A few mines remain reasonably 'dry'. On the other hand, 'wet' mines are not uncommon. Grouting is required for serious underground flows of water.

The water that percolates through sulphide or sulphide-associated deposits may bring oxygen, among other substances, into direct contact with the sulphide ore. The sulphides react to produce water soluble salts and sulphuric

acid. The water that brought the oxygen to the ore also removes the soluble reaction products from the ore and thus permits the continuation of the reaction. When this solution appears in the mine workings, it is generally characterized by a relatively low pH, a relatively high sulphate content and an abnormal concentration of various metals. In appearance, it may be clear and colourless or it may be coloured light-yellow, dark-yellow, amber or rusty-orange. The various colours are generally due to the state of oxidation of the iron present. If, by chance, cemented backfill is used in the mine, the highly alkaline underflow from backfilled areas will perhaps mask (by neutralization) the original acid characteristics of the mine water but the acid situation within the deposit still exists nonetheless.

Underground mine water is contaminated by the mining process itself. Rock-breaking creates 'fines' that become suspended in underground flows. Trace quantities of the organics (lubricants, oils, etc.) that are associated with mining machinery frequently end up in underground water. A few parts per million of water soluble explosive materials (ammonium nitrate, etc.) are normally detected in underground flows. In fact, any water soluble substance that is taken underground for any purpose can be expected to appear, sooner or later, in the mine water.

All underground water generally flows to one or more underground sumps. The water is pumped from these collection areas to the surface for disposal.

It is important to note that in Ontario many mining operations subject their collected underground mine water to a degree of waste treatment before it is pumped to the surface. Commonly, some of the suspended solids are removed using various settling mechanisms. The pH may be adjusted for a variety of reasons (equipment protection being the main reason).

Abandoned conventional underground mines in Ontario are generally allowed to flood. Only on very rare occasions will water overflow the shaft collar. In addition, the shaft will usually be capped with concrete.

If an abandoned mine is being operated on a caretaker basis and if the workings are kept dewatered, then a continuous or semi-continuous mine water effluent can be expected. This flow is generally contaminated.

The chemical characteristics of mine water vary from mine to mine, from deposit to deposit, and from camp to camp. Since, in Ontario, a mine is almost invariably near a body of water, mine water problems are commonly expected. To go a step further, some of the mineral deposits in Ontario are being worked directly beneath large lakes. The richest known sections of the fabulous uranium deposits in the Elliot Lake district of Ontario, for instance, lie beneath Quirke Lake. Quirke Lake occupies 4,200 acres and, in places, is 1,200 feet deep. To make matters worse, in this particular location because of iron sulphides in the ore, the mine water is extremely acid (pH of approximately 2.0).

In general, therefore, mine water is a problem in Ontario. Experience has shown that mine water can be handled in at least one of the following ways:

(i) The mine water can be directed to the mill for re-use or

(ii) The mine water can be directed to the tailings area, or

(iii) The mine water can be collected and treated by itself.

Again, all three methods of handling mine water have advantages and disadvantages. All three methods are presently being used in Ontario.

In Ontario, mine water is collected and treated by itself if:

(a) the mine is located a considerable distance from the mill, or

(b) the chemical characteristics of the mine water are such that the water cannot be used as make-up in the mill circuit, or

(c) the mill is operating in closed circuit with its tailings area in order to accomplish a specific objective.

In Ontario, mine water is directed to a tailings area when:

(a) a mine is close to its corresponding tailings area, or

(b) when the mine water is not acceptable for direct use in the mill circuit, or

(c) when separate treatment of the mine water would simply force a total duplication of the tailings area decant treatment facilities.

In Ontario, mine water is directed to the mill whenever

and wherever possible. However, it must be realized that mine water can, on occasion, be grossly contaminated due to natural chemical reactions within the orebody and in the mine workings. In addition, mine water can contain residual accumulations of oil, mining machinery lubricants and water soluble explosives. Also, if mill water is used to convey coarse mill tailings underground for use as backfill, the mine water can become contaminated with the mill reagents themselves. Any or all of the above substances mentioned can, on occasion, render the mine water useless for purposes of direct re-use in a mill.

In order to soften the negative impact of the foregoing statements, it is necessary to indicate that, in Ontario, most mining operations directly or indirectly use substantial quantities of mine water in their respective mills.

Secondary Effluent Control

We now turn to SECONDARY EFFLUENT CONTROL in the Ontario mining industry. There are only two basic SECONDARY EFFLUENTS that arise as a result of Ontario mining practices. These are as follows:

(1) the tailings area (and waste rock storage area) seepage and

(2) the tailings area overflow (the tailings area decant).

In Ontario, the control of seepage from tailings areas is, in a sense, straightforward. In each case the seepage must be collected. After collection, the seepage can be handled in

one (or more) of three ways:

(i) the seepage can be treated by itself, or

(ii) the seepage can be pumped back into the tailings area, or

(iii) the seepage can be directed to the treatment facility that effects control of the tailings area decant.

Depending on local circumstances, all three methods of seepage control are used in Ontario.

In Ontario, the overflow from a tailings area generally presents a large volume liquid-waste treatment problem. Obviously, the amount of water that is required to process one ton of ore varies greatly depending on the type and grade of the ore and the mining and milling procedures that are being followed. In Ontario, as elsewhere, milling procedures vary greatly. Although the majority of the mill circuits in the Province are based on froth flotation, uranium is recovered using massive ion exchange plants while quantities of some other substances (notably iron and zinc) are being recovered in gravity plants. Circuits utilizing magnetic separation are also common.

Calculations show that, in 1971, the hardrock mines of Ontario generated an average decant flow of 800 imperial gallons per day per ton ore milled. This figure is quite accurate for the Ontario mining industry as a whole since almost every plant in the entire industry in Ontario was included in the calculations. Theoretically, as the years go by, this 800 gallon figure will decrease as a result of the continued acceleration of

government water conservation programs such as wastewater re-use. Hopefully, within a few years, the processing of one ton of ore in Ontario will result in a decant overflow of less than 200 gallons.

In Ontario, the actual physical and/or chemical treatment of tailings area overflows varies, as might be expected, from property to property. The subject of effluent control in the Ontario mining industry is covered in detail in two separate reports, both of which are available free-of-charge from the Ontario Ministry of the Environment. The first report is entitled "The Problem of Acid Mine Drainage in the Province of Ontario - 1972". The second is entitled "Use, Characteristics and Toxicity of Mine-Mill Reagents in Ontario - 1972". Together, these two reports describe in detail the advantages and disadvantages of most of the mine waste treatment techniques that find use in Ontario.

It would be totally unrealistic to state that, in the Province of Ontario, we have managed to solve all of our outstanding mine waste treatment problems. We have not. It would be totally unrealistic to state that we expect solutions to all of our problems in the near future. We do not. We can state, however, that we do have a good understanding of the technical aspects of nearly all of our problems and, furthermore, most mine waste problems in the Province are now subject to adequate controls. Inadequate controls, however, presently exist for dissolved solids, sulphates, ammonia, cyanide, arsenic and perhaps for some of the

persistent mill reagents.

In Ontario, the pH of a mine-mill effluent should be maintained within the range 5.5 to 10.6 while individual metal concentrations in the effluent should not exceed 1 part per million.

The Ontario Mining Act states that the revegetation and/or stabilization of unused mine tailings areas is mandatory within the boundaries of the Province. As a result, under a variety of conditions, hundreds of acres of abandoned tailings have been successfully revegetated. In a sense this is a unique situation since conditions in the northern mining district of Ontario are not exactly conducive to lush plant growth. The northern growing season, for instance, is only approximately 145 days in length (210 days in the warmer south). Where young plants are concerned, the harsh climate of the north is duplicated in only a few areas of the world. During the cool, wet spring, the surface of an abandoned tailings area may be saturated with water. The summer, not uncommonly, brings daily temperatures of 100^{o} F to the immediate surface of the tailings mass. The surface layers of the mass expand and contract with the result that delicate plant tissues are sheared and crushed. Also, during the summer months, masses of toxic efflorescent salts can appear at or near the surface of the tailings areas. The winter months present temperatures below minus 40^{o} F in most areas. The tailings masses may be coated with several feet of

ice and snow. It is not surprising, therefore, that the mining industry of Ontario has gained a world-wide reputation in the field of mine waste reclamation.

FUTURE TRENDS IN ONTARIO

With regard to future environmental control in the mining industry, what trends are currently developing in Ontario?

The increasing government involvement in all phases of mining exploration and development cannot be ignored. Undoubtedly, this involvement will sooner or later result in new legislation involving mine effluent control and any or all of the following:

(a) Recycle. New legislation could require maximum wastewater re-use at all mining operations.

(b) Rehabilitation. New legislation could require the complete rehabilitation of any mining operation that is being abandoned or has been abandoned. In other words, the headframe, the mill and all associated buildings would have to be completely dismantled. Tailings areas, dams, garbage dumps, waste and/or spoil piles would have to be recontoured and revegetated. All old and/or abandoned mine-mill equipment would have to be removed from the property or be disposed of on the property in an acceptable manner. All visible mining excavations including open pits would have to be rehabilitated in some manner. With regard to this point, it is interesting to note that most open pits will at least partially fill with water after they have been

abandoned. A small and perhaps useful lake will have been created.

(c) Tailings Dams, Tailings Areas. New legislation could limit the height of tailings dams and could require new tailings areas to be at least a minimum specific distance from major public roads, townsites and main water supplies etc. New legislation could designate revegetated tailings areas as "not suitable" as grazing areas or as a source of feed for domestic animals. The reason for this is the suspected abnormal metal uptake by plants growing on such areas.

It is probable that, in Ontario, the relatively near future will be characterized by radical changes in mine waste treatment philosophy and technology. The key phrase may well be "treatment without chemicals". Mechanical aeration, recycle and processes such as reverse osmosis will be accentuated. Old reliables such as lime treatment will be slowly phased out. New emphasis will be placed on residual mill reagent concentrations and nutrient concentrations in mine-mill effluents and on the total oxygen demand of mine-mill wastes.

Mining has never been a provincial, state, federal or national industry. Mining has always been and will always be an international industry. Similarly, mine waste control should not be just a local or national goal. The environment does not recognize boundaries that exist only in the minds of men. Mine waste control should be and must be an international goal. Not all of

what we have learned in Ontario is applicable in the arid or barren regions of North America. But some of it is. Conversely, not all of the technology that has been developed in the arid or barren regions of North America is applicable to the problems found in Ontario. But some of it is.

Environmental control is only one of the many problems that the mining industry must face today. Present technology, however, is such that many environmental problems have been defined but few have been completely solved. It is therefore necessary for the public, the government and the industry to work together to achieve satisfactory control of pollution problems arising from mining operations.

ADVANCEMENTS IN THE TREATMENT OF ACID MINE DRAINAGE IN THE PROVINCE OF ONTARIO

by

John R. Hawley

A lecture presented at the
Haileybury School of Mines,
Haileybury, Ontario, June 1973.

Introduction

The problem which is now referred to as "acid mine drainage" or more simply "acid drainage" was known in North America as early as the year 1698. However, since acid drainage was almost invariably associated with coal mining operations, little thought was given to the amber wastes that were routinely discharged from sulphide mining operations in non-coal mining areas.

From the late 1600's to the late 1960's almost nothing was added to man's knowledge of the causes, symptoms and cures of the acid drainage that occurred in hardrock mining areas. Indeed, until 1968, the magnitude of the problem in Ontario and in Canada as a whole was not even suspected. Subsequently, we now know that acid drainage is a potential problem at any mining property where iron sulphide minerals are associated with the ore or with the waste rock.

The Chemistry of Acid Mine Drainage

Iron sulphide minerals occur in many sulphide ore deposits. Unfortunately, when these minerals are exposed to our atmosphere (oxygen, moisture, bacteria) they tend to be unstable. Their decomposition results in the formation of sulphuric acid and iron salts. The chemistry involved may be simply represented as follows:

(1) $2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$

iron sulphide insoluble	water	oxygen	ferrous sulphate soluble	sulphuric acid

(2) $4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$

ferrous sulphate soluble	sulphuric acid	oxygen	ferric sulphate	water

(3) $Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$

ferric sulphate soluble	water	ferric hydroxide insoluble	sulphuric acid

Iron sulphide minerals are rarely 100 per cent pure. They frequently contain significant quantities of other metals. Cobalt and nickel, for example, can substitute for iron in the iron sulphide lattice. As a result, when an iron sulphide mineral undergoes chemical decomposition, iron is not the only metal released to the environment. In addition, the sulphuric acid released as a result of iron sulphide decomposition promotes conditions which force many other metal sulphide

minerals into solution. The resultant solutions can be highly contaminated. In Ontario, for instance, the following substances have been commonly detected in acid mine drainage flows:

copper	nickel	vanadium
zinc	manganese	
cobalt	chromium	

The outstanding characteristics of a normal acid mine drainage flow are as follows:

(1) a low pH

(2) a high sulphate content

(3) an abnormal concentration of various metals.

The iron compounds contained in acid flows frequently impart a yellowish or amber colour to the flows. Stagnant pools of acid waste may be blood-red or deep reddish-brown in colour. In comparison, fresh acid flows emerging from the base of a tailings mass may be colourless and crystal clear.

In general, acid mine drainage flows can be generated whenever water comes into contact with iron sulphide bearing ore, waste rock or tailings.

SOURCES OF ACID WATER

There are two major sources of acid water at any property that is experiencing acid conditions. These are:

(1) the mine and its associated facilities and

(2) the tailings disposal area and its associated facilities.

(1) THE MINE

Natural surface water percolates into most mine workings at rates which are almost impossible to predetermine. Rain and snow fall directly into open pits. In most cases, this natural water comes into intimate contact with any exposed sulphide minerals that occur in the orebody or in the associated waste rock. Obviously, it is somewhat easier to predict the amount of natural water that will gain access to an open pit than it is to predict the amount of natural water that will gain access to underground mine workings. In northern Ontario, for instance, we normally expect that each acre of land will receive a daily average of 1,800 Imperial gallons of water due to natural precipitation. Of course, we don't know what percentage of this will leave any particular area as runoff or what percentage of this will evaporate or what percentage will be retained by the land itself. But it is obvious that a 50 acre open pit will receive an average of 50 x 1,800 = 90,000 imperial gallons of natural water per day.

In addition to natural water, we have process water that is pumped underground for mining purposes. In many cases, this aspect of underground water consumption is quite predictable. For instance, water is used underground for drilling, dust suppression, pumping, cooling, sanitation etc.

The quantity of water used in drilling operations can be predicted with reasonable accuracy on the basis of such things as manufacturers recommendations. The average water consumption per rock drill (jacklegs) varies from 0.5 to 1.0 gallons per minute and the daily quantity is a function of hours drilled per day. Typical usage for other drilling equipment is somewhat as follows:

Jacklegs - stopers - drifters	0.5 to 1.0 gallons/minute
Long hole drills	1.0 gallons/minute
Diamond drills	5.0 gallons/minute

Drilling time can be computed from the diamond drilling experience which normally precedes the exploitation of any ore body. From the exploration drilling and subsequent to the selection of the mining system it should be possible to forecast the drilling hours required for:

(a) development footage

(b) stope development footage

(c) production drilling footage

Water usage for the purposes of dust suppression can be determined on the basis of:

(a) the number of rounds taken per day

(b) the number of transfer points in the ore transportation system.

(c) crushing plant installation and ventilation.

(d) general allowances for hose clean up and geological examinations, and

(e) ventilation humidity requirements.

With regard to pumping, the water requirement relates to gland water and is more or less directly dependent on the number of pumps being used, the size of the various pumps and the operating pressure of the pumps.

The amount of (cooling) water used underground for regulating the bearing temperature on equipment such as crushers, fans and compressors can be accurately predicted on the basis of manufacturers specifications.

In many instances, a predictable volume of water may be used in mines where underground sanitary facilities are provided. This volume of water is more or less directly related to the number of manshifts in any given period.

Where backfill is used in a mine, water (generally mill water) will be used to convey coarse tailings from the mill to the underground workings.

In summary, the natural water that percolates into a mine (open pit or underground) and the water that is deliberately pumped into an open pit or underground for process use comes into contact with the iron sulphide bearing rock. Usually this will result in typical acid mine water. This water must be removed from the mine or the mine would flood. The water is therefore collected in one or more sumps and is pumped to the surface (or out of the pit) and constitutes a

major waste treatment problem. Incidentally, this water, while it is resident in the mine is contaminated by the mining process itself. It may contain quantities of mine-machinery lubricants, trace quantities of various explosives, rock-fines, mine-water treatment chemicals, and indeed, traces of all of the chemical materials that are used in and around a mine. If mill water is used to convey tailings underground for use as backfill, then the mine water can also become contaminated with all of the reagents that are used in the mill. Since backfill is not used in open pit operations, the overall chemical characteristics of mine water from open pit and from underground operations tend to differ somewhat.

(2) THE TAILINGS DISPOSAL AREA

The tailings area is the most obvious source of acid waste flows. The chemical/bacterial reactions that go on underground in a mine to produce acid mine water are also operative in tailings areas that contain significant quantities of iron sulphide minerals. These minerals, at the present time, are rejected as waste in most sulphide milling circuits. Since these circuits do not operate at 100 per cent efficiency, minor quantities of ore sulphides also gain access to the tailings areas and, under acid conditions, some of these sulphide minerals also break down to form water soluble substances.

In essence, two different types of acid flows or flows with potential acid producing qualities are known to originate in a sulphide type tailings area. These are:

(1) the tailings area decant (the main overflow) and

(2) the tailings area seepage (underflow from the dams etc.)

It is easy to see why tailings area seepage is contaminated. Many "reactive" minerals within the tailings mass break down to form water-soluble compounds. Water ponded on the area and rainwater etc., percolate down through the tailings mass and take the water-soluble salts into solution. This contaminated water emerges at the bases of dams as seepage. Since natural precipitation (rain, snow) is a prime feedwater for the seepage process, tailings areas that have been abandoned for decades will, in many cases, still produce large volumes of acid seepage. The following is an actual example of the chemical characteristics of an acid seepage flow:

pH	2.0
Sulphates as SO_4	7,440 ppm (parts per million)
Acidity as $CaCO_3$	14,600 ppm
Ferric Iron as Fe	1,450 ppm
Ferrous Iron as Fe	1,750 ppm
Uranium as U	7.2 ppm
Zinc as Zn	11.4 ppm

Nickel as Ni	3.2 ppm
Cobalt as Co	3.8 ppm
Copper as Cu	3.6 ppm
Manganese as Mn	5.6 ppm
Aluminum as Al	588 ppm
Lead as Pb	0.67 ppm
Cadmium as Cd	0.05 ppm
Lithium as Li	0.07 ppm
Vanadium as V	20 ppm
Silver as Ag	0.05 ppm
Titanium as Ti	15 ppm
Magnesium as Mg	106 ppm
Calcium as Ca	416 ppm
Potassium as K	69.5 ppm
Sodium as Na	920 ppm
Arsenic as As	0.74 ppm
Phosphorus as P	5.0 ppm
Chemical Oxygen Demand	270 ppm

The decant overflow of a tailings area is a very important waste flow as long as the mill associated with the tailings area is operating. If the tailings area is abandoned, the decant overflow may or may not be of importance.

The decant overflow at an active mine-mill operation mainly consists of discarded mill process water and the natural

runoff collected by the tailings basin itself. Discarded mine water may or may not form part of the decant overflow.

Decant overflows at sulphide mines are generally contaminated by the following:

(1) suspended solids

(2) mine-mill reagents (the chemicals used in mining and milling the ore)

(3) water soluble acid-producing salts collected from exposed masses of tailings by natural runoff and

(4) partially oxidized sulphur compounds (formed during the milling of iron sulphide minerals).

The storage of waste rock or low grade material at a sulphide mining operation also presents a problem. These waste piles are frequently washed by rain or meltwater and the available acid producing salts go into solution. The underflow from these piles is frequently quite contaminated. The same process is operative when sulphide-bearing waste rock or low grade material is used for general construction purposes such as road building.

CHEMICAL WASTE TREATMENT

Neutralization is, at present, the most widely accepted form of treatment for acid drainage flows. There are only five readily available neutralizing reagents. These are:

(1) ammonia
(2) sodium carbonate
(3) sodium hydroxide
(4) limestone and
(5) lime.

Of the above, ammonia should not be used since it displays undesirable environmental effects. Limestone is generally not used since it cannot, by itself, produce the highly alkaline solutions that are necessary for optimum metals precipitation. Lime, because of its low cost and great versatility, is widely used. Sodium carbonate also enjoys fairly wide usage. Sodium hydroxide is an acceptable neutralizing agent but, at the present time, it tends to be expensive and it does have certain undesirable corrosive properties with regard to equipment and handling.

The chemistry of the neutralization reactions of all of the listed reagents are somewhat similar. For example, the chemistry of lime neutralization is as follows:

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O + \text{heat}$$

slaked lime	sulphuric acid	"insoluble" calcium sulphate	water

The metals in solution react as follows:

$$2FeSO_4 + 2Ca(OH)_2 \longrightarrow 2Fe(OH)_2 + 2CaSO_4$$

soluble ferrous(iron) sulphate	slaked lime	"insoluble" ferrous (iron) hydroxide	"insoluble" calcium sulphate

The "insoluble" precipitates that result from the neutralization reaction settle to form a watery sludge that, in itself, presents a handling problem.

Briefly, the main environmental problems associated

with the use of neutralizing reagents for the control of acid drainage are as follows:

(1) The voluminous watery sludge that is produced as a result of the neutralization reactions can be of varying degrees of stability. If this sludge (largely composed of calcium sulphate and various metal precipitates) is not properly handled (a subject in itself) then the metals can go back into solution and nothing has been accomplished.

(2) Although the neutralization reactions result in a treatment plant overflow that has desirable characteristics with regard to pH and metals concentration, the overflow does contain an increased "total dissolved solids" concentration as well as increased concentrations of the metals and non-metals that form the neutralization reagents themselves. Admittedly these metals are rather innocuous as far as their toxicity is concerned but the overall concept of replacing a severe form of pollution with a less severe form of pollution is not a good concept. It just happens to be a practical concept.

(3) Acid mine drainage conditions at a sulphide mining property can and may persist for decades after the property has been abandoned. As such, if neutralization was the method chosen to combat acid drainage at the property,

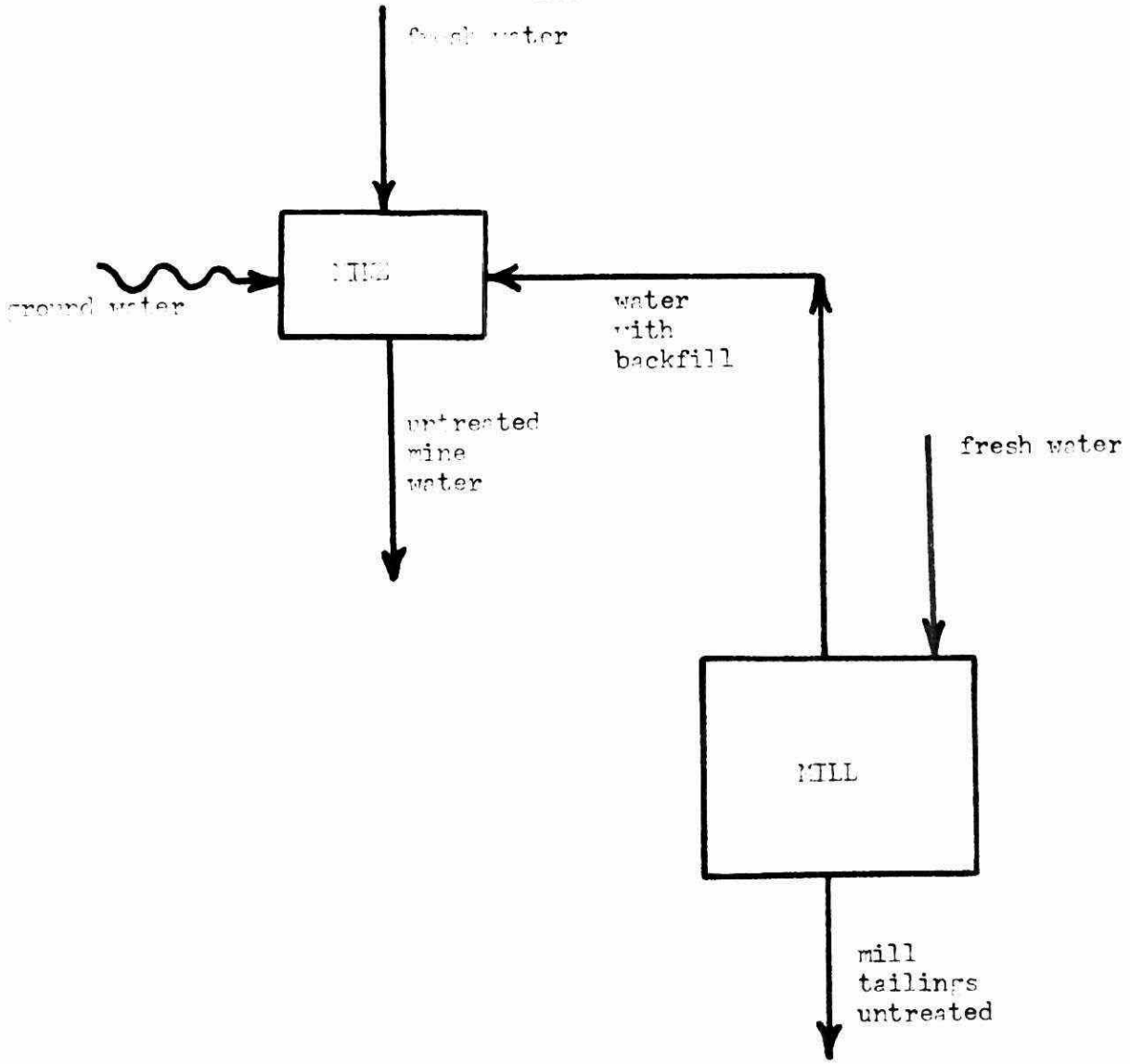
this neutralization must be continued for decades after the property has been abandoned. This, of course, presents great problems with regard to treatment plant maintenance, effluent monitoring, bulk transport and storage and continuous feeding of reagents, sludge disposal and continuous operation during the cold months.

Fortunately, mine waste treatment technology is proceeding in a direction that is allowing us to ignore the neutralization processes to a greater and greater extent and still achieve an acceptable degree of acid control.

In Ontario, mine waste control technology has developed in the following manner:

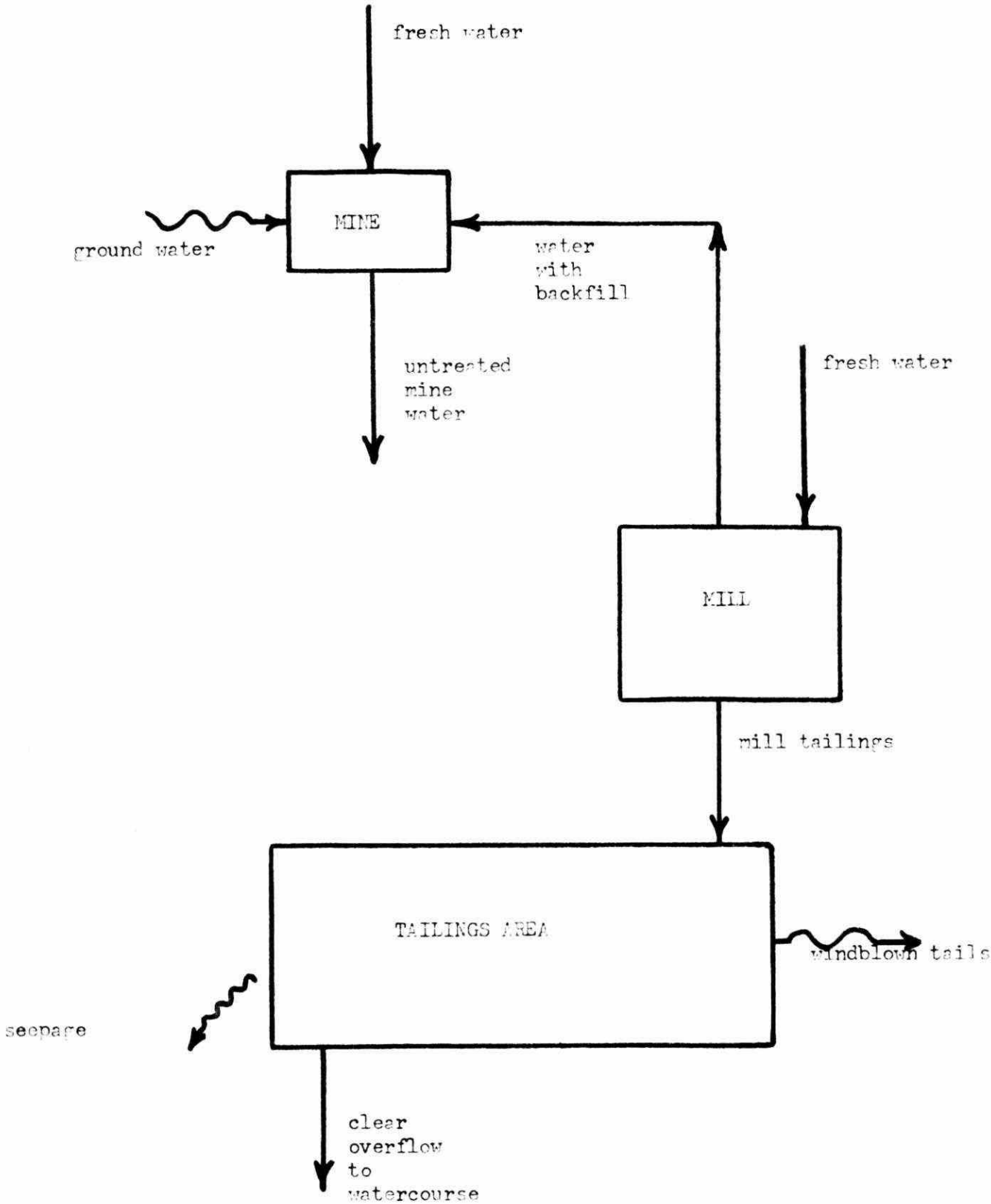
STAGE I (pre-1957)

In the early days of mine waste control technology in Ontario, only fresh water was used in most mines and in most mills. Contaminated minewater was discharged untreated to the nearest watercourse or natural depression. The tailings slurry from the mill was generally directed untreated to the nearest lake or large natural depression. Tailings dams were rare. Either freshwater or millwater was used to repulp tailings for use as underground backfill.



STAGE II (1957 - 1967)

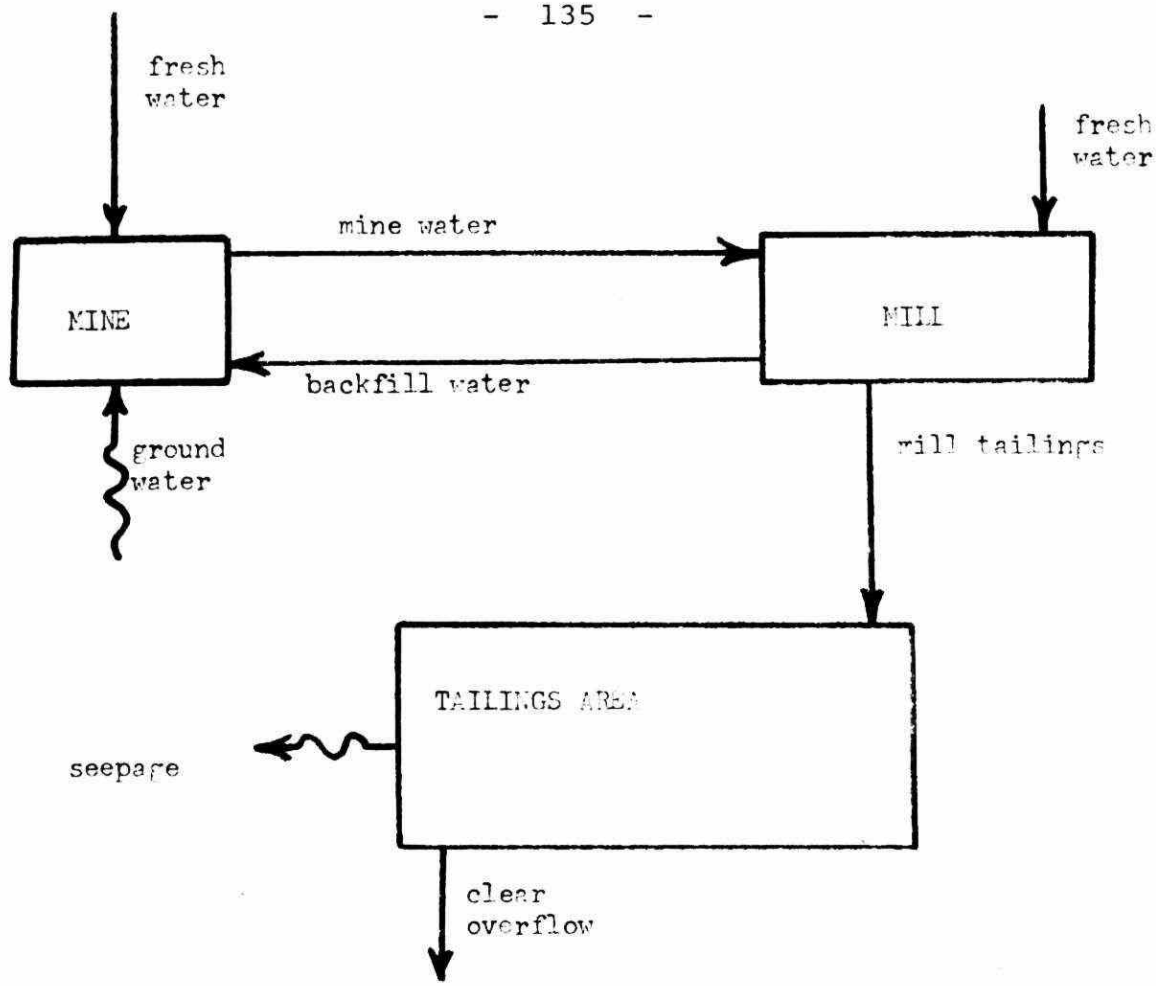
Public awareness of the activities of the mining industry brought about Stage II of mine waste control in Ontario. The concept of suspended solids pollution was introduced and, as a result, the tailings dam and formal tailings area came into existence. All other aspects of mine waste control remained as in Stage I.


fresh water
MINE
ground water
water
with
backfill
untreated
mine
water
fresh water
MILL
mill tailings
TAILINGS AREA
windblown tails
seepage
clear
overflow
to
watercourse

In stage II, most solids were retained within the boundaries of the formal tailings area. The dams were designed to promote seepage. Seepage, dam stability and windblown tailings became problems of varying magnitudes. Towards the end of stage II, the Province of Ontario had successfully promoted the revegetation or stabilization of non - sulphide bearing tailings areas. Windblown tailings and to some extent seepage associated with these areas became minor problems. Tailings area failures were common but almost always occurred in remote areas which received little public attention.

STAGE III (1968 - 1970)

During this period, acid mine drainage was identified as a major environmental problem in many Ontario mining camps. The government increased its mine waste monitoring activities and legal action (primarily on the basis of pH and solids) involving mining companies became routine. Minewater was recognized as a contaminated waste flow and, as such, chemical and/or physical treatment of minewater became routine. Most minewater discharges were re-directed to the mill for use as make-up water. The fresh water requirement for an average mill dropped since minewater was being re-used in the mill.



STAGE IV (1970 - 1973)

During the past three or four years, the following major advances in mine waste treatment technology have been made:

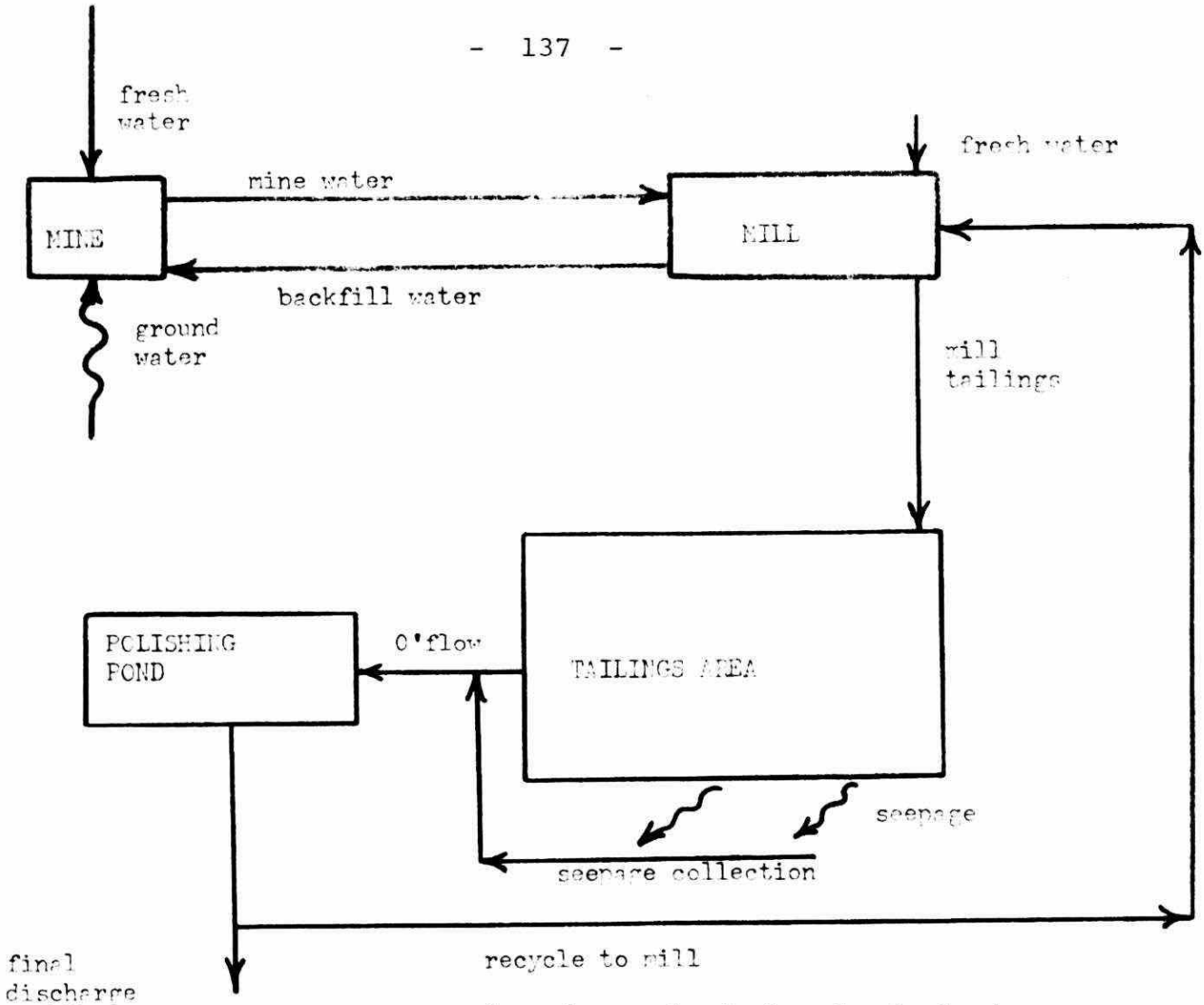
(1) The use of new analytical techniques has resulted in the identification of many previously unsuspected contaminants in mine waste flows. As a result, the use of waste treatment processes such as neutralization and metals precipitation have become common.

(2) Tailings area seepage was recognized as a major problem at most sulphide mining operations. All such seepage is now collected, treated and returned to the tailings area or collected and directed to the main waste treatment facility.

(3) In order to facilitate chemical waste treatment processes, to provide a steady source of recycle water and, in general, to act as an effluent polishing unit, a secondary treatment facility (an engineered lagoon) has been added to most sulphide tailings areas. This lagoon (pond) receives the clear overflow from the tailings area and generally also receives any seepage that has been collected from the bases of permeable dams.

(4) All new operations are now expected to direct tailings area overflows back to the mine-mill processes for re-use in the various circuits and operations. As a result, fresh water requirements for sulphide-type operations have dropped and the volume of waste water that must be finally discharged to a natural watercourse has dropped.

(5) Government control has increased with regard to tailings area construction, mine-mill effluent characteristics, and revegetation or stabilization of abandoned areas. As a result, major tailings area failures are now almost unknown and minor tailings area failures are uncommon. Revegetation programs are beginning to show signs of success. Most mine-mill effluent flows are now adequately controlled.



(6) A government program has determined the chemical characteristics and toxicity of most of the chemicals used in mine-mill circuits. Many treatment systems have been adjusted to enhance the natural breakdown of these reagents before discharge to a watercourse. Tailings areas and secondary lagoons are now also sized to ensure the complete oxidation of unstable acid-producing sulphur compounds.

(7) Uncontaminated runoff water and natural streams etc., are now diverted away from sulphide bearing tailings areas in order to prevent the unnecessary contamination of such waters and the ensuing requirements for waste treatment.

The use of lake basins for tailings disposal is now actively discouraged by the government although, under exceptional conditions, lake disposal has been permitted.

Currently Developing Advancements in the Control of Acid Drainage from Hardrock Sulphide Operations

(1) The collection and treatment of contaminated seepage from both active and abandoned properties is a current major problem. The problem has its origin in the simple fact that the tailings dams of today are generally being built to encourage seepage (for structural reasons). The obvious solution to the seepage problem is to build impermeable dams. This trend is developing.

(2) At active and more particularly at abandoned sulphide properties, the acid drainage from the tailings area itself is the major problem. If the iron sulphide minerals were not present in an abandoned tailings area, an acid problem would not exist and long-term waste treatment would not be required. Separate recovery and subsequent separate storage of iron sulphide minerals is now recommended. The iron sulphide storage area should not present major water treatment problems. Revegetation of the main tailings area (which is required in Ontario) is a relatively simple task when acid producing (or alkaline producing) substances are not present.

(3) Current thinking places great emphasis on the types of mine waste treatment that do not involve massive chemical additions to the waste being treated. Mine and mill water re-use, iron sulphide segregation, natural aging of effluents and mechanical aeration all fall in this category. Associated concepts are revegetation of exposed areas, the construction of impermeable dams, the diversion of uncontaminated natural waters and careful selection of mine-mill reagents. When these concepts are applied, the amount of freshwater required to sustain a mine-mill operation is minimized, the amount of water-born waste that is ultimately discharged is minimized and the overall effect of the mining operation on the environment is minimized. This approach, of course, centres around the conservation of renewable and non-renewable natural resources and brings a mining operation as close to harmony with nature as is presently possible. The basic concept of the approach is that it is easier to prevent an acid mine drainage problem than it is to cure it.

In the near future, it is expected that the overall problem of acid mine drainage will come under complete control. Perhaps the use of sodium silicate will give us very stable and dependable sludges. Perhaps investi-

gations into the use of the natural clay bentonite will result in low cost methods of constructing impermeable tailings dams. Perhaps a thorough search for acid resistant vegetation will produce a species that thrives on sulphide saturated tailings masses. Perhaps the electrogalvanic nature of the various sulphide minerals themselves will suggest to us methods of accelerating or retarding the selective leaching of sulphidic tailings areas. Perhaps breakthroughs in the field of bacteriology will teach us to understand and to control what we formerly did not understand and could not control.

Acid mine drainage from hardrock sulphide mines is no longer the elusive phenomena that it was six years ago. At the present time, acid mine drainage is a difficult but adequately understood waste treatment problem. Its solution at any particular location is largely dependent on local geography and economics. But its solution does exist.

HYDROMETALLURGY Vs. PYROMETALLURGY

TODAY AND TOMORROW

by

John R. Hawley

A lecture presented at the
Haileybury School of Mines
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INTRODUCTION

Extractive metallurgy can be divided into three basic categories:

(1) pyrometallurgy (fire metallurgy)

(2) electrometallurgy (electric metallurgy) and

(3) hydrometallurgy (water metallurgy).

At the present time, civilization as we know it is all but totally dependent on the processes of pyrometallurgy and electrometallurgy. Without this technology we could not hope to meet our current national demand for such things as iron and copper. We have to have iron and copper to survive but to an even greater extent, our survival depends on the condition of our environment. Unfortunately, there are some very serious environmental problems associated with some pyrometallurgical operations. In response to a strong anti-pollution sentiment, industry and government have begun to investigate alternatives to pyrometallurgy. The most promising alternative is hydrometallurgy.

At the present time very few people have an in-depth knowledge of hydrometallurgy. Its widespread acceptance by the general public is based on the fact that somewhat extravagant claims have been made to the effect that hydrometallurgy is a process that does not give rise to pollution. This, of course, is not true. The facts are that hydrometal-

lurgy is not a single process but instead is composed of hundreds and perhaps thousands of processes that are all water-based. Some hydrometallurgy processes are essentially pollution-free but there are many that pose significant environmental problems.

The concepts of hydrometallurgical operation can be applied to all phases of mining, milling, smelting and refining and for this reason it is necessary to look closely at each use of hydrometallurgical technology before hydrometallurgy as a whole is labelled "non-polluting".

HYDROMETALLURGY DEFINED

Hydrometallurgy is the science and technology of extracting and recovering metals chemically from ores by the use of aqueous solutions, as distinct from pyrometallurgy which comprises smelting and other similar high-temperature operations. The principles involved in hydrometallurgy are those of physical chemistry, inorganic chemistry, electrochemistry and analytical chemistry: indeed, the production of metals by hydrometallurgy can be broadly described as extensions of these principles on a commercial and economic scale. The procedures commonly employed in hydrometallurgical operations represent combinations of the techniques used in mineral dressing, chemical engineering and electrochemical technology.

The operations involved are:

(1) the dissolution of a metal or metal compound by a suitable lixiviant (water alone or with added reagents) usually termed leaching,

(2) the separation of waste and purification of the leach solution, and

(3) the precipitation of metal from the leach solution by chemical or electrolytic means.

Developed initially at the turn of the 20th century for recovering gold from low-grade ores, the technology of hydrometallurgy has been improved by such procedures as ion exchange, solvent extraction, distillation and high-pressure, high-temperature leaching. These processes are now recognized as conventional operations.

For those who think that hydrometallurgy does not presently find widespread use, consider the following: Hydrometallurgical techniques are used wholly or in part to produce, in commercial form, all but six or seven of the eighty-two known metallic elements.

HYDROMETALLURGY APPLIED TO UNDERGROUND MINING

In conventional underground mining, openings are constructed to penetrate the orebody and its surrounding rock.

The ore is broken and is then transported to the surface for treatment. Although this process is efficient in that the entire orebody can sometimes be removed, enormous quantities of waste material must generally be removed along with the ore minerals. The waste material, in the form of tailings, must be disposed of on the surface. The improper disposal of tailings can give rise to serious environmental pollution. In addition, contaminated mine water also presents a serious disposal problem. Some mining methods are such that pillars of ore are left underground. In these cases the ore may never be recovered and, as such, a non-renewable natural resource has been wasted.

Hydrometallurgy does present an alternative to conventional underground mining. In its simplest application, water alone is pumped into a mineral deposit. The water releases the desired substance from the ore and, when chemically or physically saturated with the substance, the water is pumped back to the surface where the required substance is separated from the water. Much of our common salt is mined this way. In salt mining, the process involves drilling a hole to the salt deposit which may be at a depth of a few hundred to a few thousand feet. The hole is then cased with a steel piping to the top of the deposit and a pipe is lowered through the casing to the bottom of the deposit thus creating a deep well with two fluid passages.

Water is pumped down to the deposit where it dissolves the salt, forming brine, which is then pumped to the surface. At the surface, the salt is recovered from the water by evaporation.

Another important natural substance that is recovered by pumping water underground is sulphur. Super-heated water is pumped underground into a sulphur-bearing formation. The sulphur melts and, with the assistance of compressed air, is forced to the surface where it hardens into a solid mass. The amount of hot water required to melt one ton of sulphur varies from roughly 1,000 to 12,000 gallons depending on the characteristics of the formation being mined.

Potassium salts, on occasion, are also mined by injecting water into potassium-bearing strata.

Even the simple concept of solution mining is not without its problems. For instance, when massive deposits of substances such as salt and sulphur have been removed via the methods described, the overlying rock is left unsupported. Land subsistence in the area can rupture the pipes through which production is achieved and can disturb and can possibly cause the contamination of local water supplies. The solutions being recovered from the deposits may become contaminated or otherwise unacceptable for industrial use and, as a result, may form a liquid waste

disposal problem on the surface.

The chemical and physical characteristics of sodium chloride, the potassium salts and elemental sulphur are such that fresh water alone can be used to effect their recovery. Sodium chloride and the potassium salts are soluble in fresh water and elemental sulphur melts at a relatively low temperature (water is used to convey heat to the sulphur deposits). On the other hand, most Ontario metal ores (iron, copper, lead, zinc, gold, silver, nickel, cobalt etc.) are not very soluble in water and do not melt at relatively low temperatures. Therefore, simple fresh water mining of the majority of our metal deposits is impossible.

For hundreds of years, man has known that certain water-soluble substances have the power to dissolve many of the common metal ores. Such a substance is sulphuric acid. We are currently examining the possibility of pumping such substances (in aqueous solution) into ore deposits in order to liberate and recover the contained metal values. Termed "in situ leaching", this operation is really just a hydrometallurgical extension of the basic concept of fresh water solution mining. The point that must be made is that, at the present time, in situ leaching in its strictest sense is in its experimental stages. Actual commercial applications of in situ leaching (again, in its

strictest sense) are almost unknown.

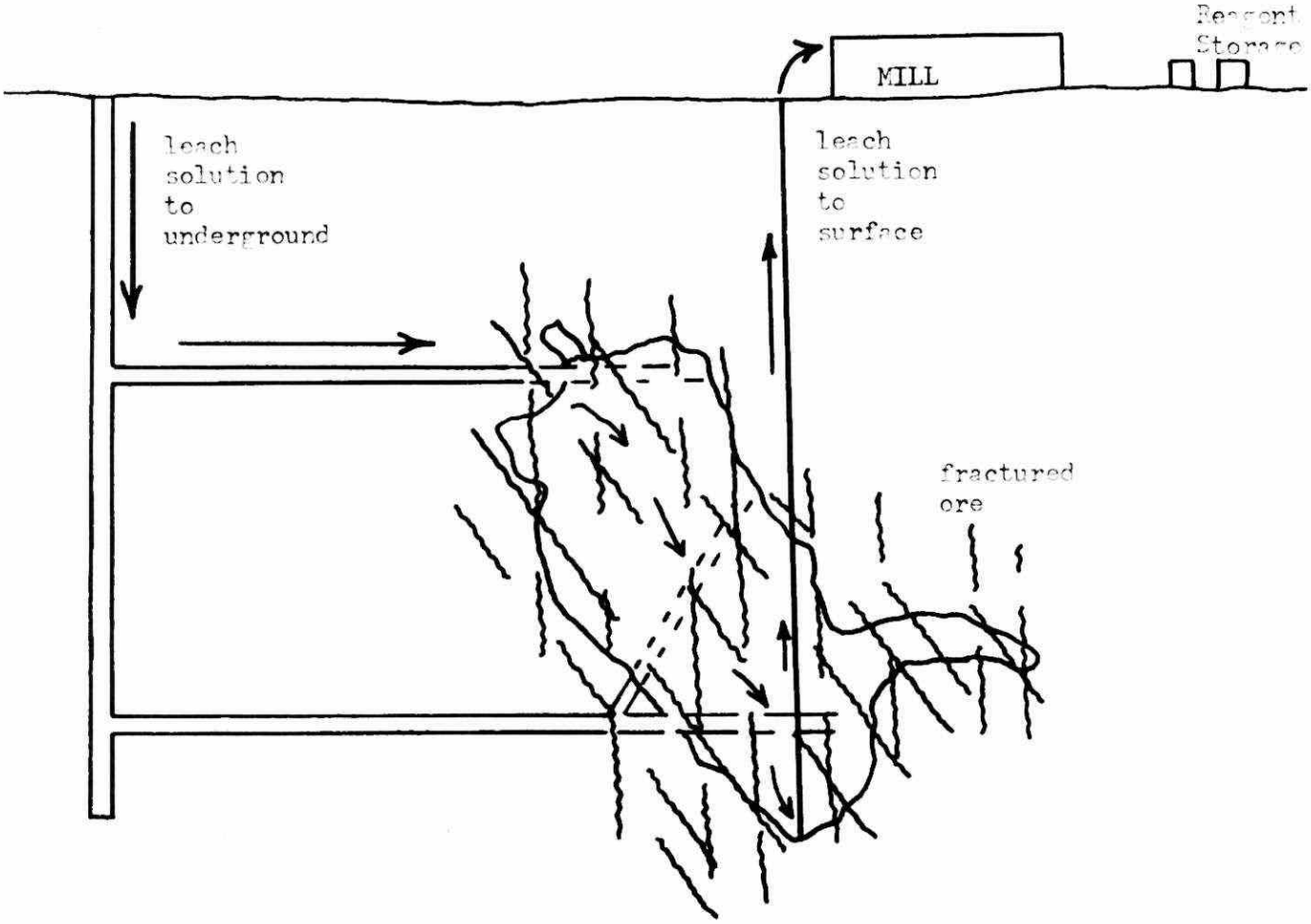
The potential environmental advantages of in situ leaching are obvious. The leaching solutions pumped underground to the ore should be designed to take only ore minerals into solution. If this can be done, the siliceous and other non-reactive gangue which today constitutes the bulk of our tailings disposal areas on surface will be left underground. Tailings areas as we now know them would be eliminated. The importance of this can hardly be overestimated. In situ leaching, of course, would also eliminate conventional underground mining operations along with crushing and grinding operations in the mill. There would be no energy requirements for mine ventilation, hoisting, lighting, drilling, and waste and ore conveyance etc. There would be no underground work force and a permanent headframe with its attendent facilities would not be required.

In situ leaching does, of course, present some very real technical and environmental difficulties. The foremost of these has to do with the fact that in situ leaching is primarily a chemical or chemical-based reaction. In other words, the leach solution must be brought into contact with every ore particle in the orebody if, indeed, every ore particle is to be recovered. This can only occur

if the orebody is very highly fractured. Most orebodies are fractured to some degree but almost never to anywhere near the degree required to make in situ leaching practical. Obviously a practical method of uniform orebody fragmentation has to be developed before in situ leaching becomes commonplace. One American company has made application to detonate a 20-kiloton nuclear device in a low-grade copper deposit some 1,200 feet below ground level. The blast is intended to crush the ore creating a chimney through which copper could be recovered by in situ leaching with aqueous sulphuric acid. If nuclear devices are to be commonly used in this manner, the environmental side effects will have to be calculated very carefully. Large non-nuclear fragmentation charges would have to be placed very carefully around and within the orebody. As a result, one or more shafts and at least limited crosscutting and drifting would have to be carried out unless such charges could be put in position from surface using very large diameter drill holes. There is always the chance that a large explosive charge could set a deposit of massive sulphides on fire. This perhaps would not be bad from a leaching standpoint (it may be a definite advantage) but it would be a disadvantage from an environmental standpoint. The fire could be put out by flooding the fragmented deposit but this could take weeks, months or

perhaps years. In the meantime, copious amounts of sulphur dioxide would escape to the atmosphere. Another concern involves the migration of leach solution away from the fragmented ore deposit. High volume migration from the deposit could have very serious environmental effects. Also, the loss of large volumes of leach solution would make the operation uneconomical.

In situ leaching is obviously uneconomical when the ore deposit contains significant amounts of leach-reagent consuming substances other than the ore minerals themselves. One other problem that may plague in situ leaching circuits is the progressive "poisoning" of leach liquors by leach-reagent soluble substances that occur in the ore or waste rock. These unwanted substances could build to such high levels in the leach circuit that the overall chemistry of the circuit would be affected. The solution to this problem is to bleed off a portion of the barren liquor discharge from the mill and to dispose of it on the surface rather than returning it underground. Sophisticated waste treatment could be required in order to stabilize the bleed off.



In situ leaching would be best applied, at the present time, to low grade deposits which could not be economically mined by conventional means. It is difficult to estimate the % recovery that one could expect from in situ leaching but it is probable that recoveries would be low due to the coarse fragmentation of the ore. As fragmentation techniques improve, ore recoveries would also improve. If in situ leaching was applied to tailings masses, the expected recovery would be high due to the very fine fragmentation of the tailings mass itself.

A modified form of in situ leaching has found use

in Ontario. The mined out stopes of Ontario's Elliot Lake uranium camp still contain considerable amounts of uranium. Some of it is too low-grade to be mined by conventional methods. Higher grade ore remains as pillars that are required to support the roof of the mine. It was found that a strain of bacteria, called thiobacillus ferro oxidans, which naturally exists in the mines, had a capacity to actually leach uranium from the rock in the mine. In reality, the bacteria have little to do with the uranium itself. Instead, they derive their energy by feeding on the (ferrous) iron of the pyrite which is associated with the uranium ore. The ferric sulphate that results attacks the tetravalent uranium in the ore body and oxidizes it to the hexavalent state which is soluble in dilute sulphuric acid (also believed to be a by-product of the activity of the bacteria). The resulting soluble uranium salts coat the exposed underground rock surfaces of the mine. Acid mine water, under high pressure, is sprayed on the exposed rock surfaces and takes the uranium into solution. The mine water is collected and directed to the mill (on surface) where the uranium is recovered. One mine in the area is known to have maintained a steady production rate of 10,000 to 12,000 pounds of U_3O_8 per month from mine water with a grade of .24 pounds U_3O_8 per ton and a pH of 2.3. Obviously,

minewater from this type of operation is highly contaminated. Under no circumstances should it be discharged untreated into a natural watercourse.

As we have seen, in Ontario, in situ leaching in its strictest sense has no present or apparent near future application as far as base metal production is concerned. Solution mining for common table salt will continue to be important. The in situ leaching of abandoned uranium stopes will continue on a limited scale.

It should be obvious by now that hydrometallurgical mining is not a pollution-free method of underground mining.

HYDROMETALLURGY AS APPLIED TO MILL PROCESSING

At the present time, we are faced with the fact that most ore is being recovered using conventional underground mining methods. The coarse broken ore is hoisted to the surface for treatment. Once on the surface, the ore can be treated in a variety of ways. Conventional milling circuits require that the ore be very finely divided since each individual ore particle must be cleanly liberated before it can be recovered. A great deal of energy and money is therefore spent in crushing and grinding our ores to a sand or powder consistency. In some cases, hydrometallurgical technology permits us to avoid the fine grinding which is generally required. Some ores are amenable to vat (or heap)

leaching.

In very simple terms, vat leaching is accomplished by bringing a leach-solution into contact with broken ore that is sitting in large vats. The metal in the ore transfers to the leach solution and is subsequently recovered by chemical or electrical means. One of the main advantages of this hydrometallurgical route is that only coarse crushing of the ore is generally required. At one operation in Chile, for example, the ore was crushed to about 1 centimeter maximum diameter and charged into tanks with filter bottoms. Each tank held as much as 11,000 tons of ore per charge. Several tanks were operated in series with fresh sulphuric acid leach solution from associated electrolytic cells being fed to a tank containing nearly spent ore. The leach solution percolated through the interstices in the charge and passed through the filter bottom. The filtrate was collected and discharged into the next tank etc., until in the final tank the copper-bearing leach solution was brought into contact with the fresh ore. The leaching cycle required about four days after which the liquor was drained from the spent ore. The spent ore was washed with dilute water solutions and then removed from the tank and discarded. By changing the flow of leach liquors, each ore tank was in turn filled, leached, washed, and then the spent

ore was discarded. The pregnant leach solution itself contained some cupric chloride which resulted from the dissolution of small amounts of copper chloride in the ore. To reduce the chlorine content, the solution was passed through towers containing metallic copper which reduced the cupric chloride to insoluble cuprous chloride which was removed by settling and filtration. The purified solution was electrolyzed in mastic-lined, reinforced concrete cells, each of which contained 60 to 70 lead-antimony anodes. The cells, of course, recovered the copper as copper metal. The solution entering the cells contained about 3% H_2SO_4 which was increased to 6% by electrolysis and then returned to the leaching plant to treat a succeeding batch of ore.

At this particular plant, over 200,000 tons of copper was recovered annually from an ore containing 2% copper (90% of which was present as oxidized copper).

The process described above is fairly typical of vat leaching processes. From an environmental standpoint, several points can be made:

(1) assuming that vat leaching techniques can be successfully applied to sulphide ores, the energy requirements of fine grinding etc., are largely eliminated.

(2) since sulphide flotation techniques do not play a part

in vat leaching and the subsequent solution processing, the complex and sometimes toxic chemicals used to achieve flotation are eliminated.

(3) vat leaching can be conducted on an almost closed circuit basis. This is an important environmental "plus" since waste discharges to the environment are minimized. However, since modern flotation technology is beginning to also utilize the concept of waste-water recycle, this may not be an extremely important factor in the future.

(4) one major point that is not particularly clear at the present time concerns the environmental effects of the tailings that would be discharged from a sulphide ore vat-leaching process as compared to the environmental effects of the tailings that are presently discharged from conventional mill processes such as differential flotation. The adverse environmental effects (example: acid drainage) that are generated by iron sulphide-bearing flotation tails are well documented. The effects are both severe and long-term. However, what is the fate of the iron sulphide minerals in a vat-leaching circuit? In general, iron sulphides will survive a vat leach and, as such, will report in the tails. Vat-leach tails, however, are quite coarse whereas

flotation tails are fine and therefore have a large surface area to stimulate natural chemical reactions. On the other hand, even through vat-leach tails are relatively quite coarse, could the leach solutions themselves increase the reactivity of the iron sulphide minerals by processes such as etching of crystal surfaces (which increases surface area) and cleaning of crystal surfaces (which removes protective coatings). In general, hydrometallurgical processes are quite capable of being more efficient than conventional mill processes. The result is that, when compared to conventional mill processes, hydrometallurgical processes would tend to lose less valuable metal to tails. Hydrometallurgical tails, on the other hand, would tend to be saturated with water soluble salts that could be readily lost to the environment. Careful washing of the tails would solve this problem.

The leach solutions that are commonly employed are chosen with a view to providing the most efficient and least expensive recovery of metals. In general, these solutions have the following characteristics:

(a) the solution should be selective to the extent that it dissolves the desired metals and does not react with valueless minerals.

(b) when added reagents are used in aqueous solution they should be such that their solubility in the solution is high enough to ensure adequate (commercial) reaction rates.

(c) the leach solution should not be reactive to the extent that corrosion of leaching vessels becomes excessive. Hydrochloric acid solution, for example, although it is a good selective solvent that can be prepared in concentrated form, is greatly restricted in use by the fact that it very readily attacks all common base metals and can thus be used only in vessels constructed of glass, stoneware, plastics or hard rubber -- all costly and weak materials.

(d) reagents should be readily available at low cost or be such that they can be easily regenerated or converted to useful by-products.

The fact that various reagents are available to accomplish essentially the same job in hydrometallurgy is an important point in the eyes of the environmentalist. Before a particular reagent is chosen for use, its overall effects on the environment as a whole should be evaluated. If the reagent in question exhibits characteristics that are not compatible with life as we know it, then a substitute should be found for that reagent. Of course, this point also

holds true for the selection of conventional froth flotation reagents etc.

What common reagents are available for use in hydrometallurgical leaching circuits? Of the acidic reagents, sulphuric acid is usually lowest in cost and most readily available, largely because it can be produced as a by-product in roasting sulphide minerals or by burning elemental sulphur in air. Also dilute sulphuric acid has the advantage that it can be easily regenerated by electrolysis or by other means; it is nonvolatile at ordinary temperatures in aqueous solutions; it is reasonably selective; it can be contained in metal or wooden vessels: and it can be prepared in any desired concentration. If sulphides are present in an ore that is to be leached, sulphuric acid can be generated by oxidation of the sulphides in situ if the leaching is carried out at a high enough temperature in the presence of oxygen.

Providing the mineral compound reacts with sulphuric acid to produce a soluble sulphate the many properties named make sulphuric acid a desirable leaching reagent. Not unexpectedly, sulphuric acid solution is used as a solvent for most of the copper, cobalt, zinc, cadmium, vanadium and uranium ores that are treated by hydrometallurgical processes.

Nitric acid finds little use as a leaching medium for ores, largely because of its volatility and its tendency

to decompose to nitrous oxides, etc., necessitating reoxidation if the acid is to be regenerated for subsequent use. The cost is much higher than that of sulphuric acid and regeneration is essential if it is to be used for treating low-grade ores. Its use is restricted to treating alloys or oxidized ores as it is decomposed with the production of elemental sulphur and sulphates when in contact with metal sulphides. It is used for "parting" gold-silver alloys, i.e., converting the silver to soluble silver nitrate and leaving the gold unattacked in the metallic form.

Hydrochloric acid is, like nitric acid, restricted in use by its tendency to volatilize. It dissolves many oxides readily and reacts vigorously with sulphides to produce H_2S and metal chlorides, but is difficult and costly to regenerate from the chlorides. The corrosive effect of chloride ions in solution as mentioned above, limits the commercial usefulness of hydrochloric acid in leaching operations. It is used, however, successfully in two important operations: (1) in combination with NaCl in a brine solution, to leach copper, zinc, cobalt, nickel, lead and other metals from pyrite residue which has been given a chloridizing roast; (2) in treating impure tin ores containing sulphides as well as cassiterite (tin oxide) to dissolve the sulphides, leaving a residue of pure tin oxide for subse-

quent smelting - a "reverse" type of leaching in which the desired metal is undissolved. Hydrochloric acid and chlorides are used in other hydrometallurgical procedures in the production of magnesium, for removal of impurities from tungsten ores and, in an unusual fashion, in the production of germanium and gallium by treating the concentrates with hydrochloric acid to produce chloride solutions. These solutions are then extracted and fractionally distilled to separate pure chlorides from which the pure metals can be prepared by electrolysis or other means.

There are several less important acidic reagents that have found restricted use, among them ferric sulphate, ferric chloride, sulphur dioxide (sulphurous acid) and hydrofluoric acid. The principal use of ferric sulphate is in leaching copper ores containing both copper oxide and copper sulphide minerals. Here a leach solution containing both sulphuric acid and ferric sulphate is employed: the sulphuric acid to dissolve the copper oxides and ferric sulphate to dissolve the sulphides. Ferric chloride has been used to leach manganese dioxide (MnO_2) from certain ores by forming soluble manganous sulphate, together with thionates and other soluble compounds. Hydrofluoric acid is used to dissolve silica from pulverized magnetite ores where the latter are to be used for iron powder manufacture and must

be substantially free of silica. These and other acid solvents are restricted in use by cost, volatility, chemical instability or other characteristics; they are used only in specific operations where the required result can not be obtained by using a cheaper, more convenient reagent.

A group with entirely different properties comprises the basic reagents - caustic soda, sodium carbonate and bicarbonate, sodium cyanide and ammonium salts in the presence of free ammonia. The general characteristic of leach solutions containing these reagents is that, differing from acid solutions, they tend to form soluble metal compounds containing oxy-anions such as CrO_4^{2-}, anionic complexes such as $\left[UO_2(CO_3)_3\right]^{4-}$ or cationic complexes of the form $\left[Ni(NH_3)_x\right]^{2+}$. Basic leach solutions do not generally react with basic constituents , such as carbonates, in an ore. Thus, if an ore contains a high percentage of carbonates, the useless consumption of acid solely to decompose (e.g., calcium carbonate) could easily reach such proportions as to make acid leaching economically impossible. In such cases basic leaching is the first and often the only choice.

Of the basic reagents, caustic soda (NaOH) is the most widely used. It is relatively inexpensive, nonvolatile, chemically stable, selective, not too difficult to regenerate and it can be prepared at any desired concentration. Thus,

where it is chemically suited, it is the preferred basic leaching reagent. Its use is limited, however, to the extraction of metals such as zinc, aluminum, silica, gallium, antimony, chromium, tungsten and other similar metals. The hydroxides of these metals are soluble in an excess of caustic soda to form the corresponding zincates, aluminates, gallates, tungstates, etc., which have various solubilities in aqueous solutions depending on the NaOH content of the solutions. Caustic soda has the added advantage that it is stable at temperatures up to 1,000^{o}C and can thus be used to fuse refractory minerals, such as those of tungsten, vanadium, chromium and others, forming the corresponding sodium salts (tungstate, vanadate, chromate, etc.) which, on cooling, can be leached with water or weak caustic solution.

Another useful and practical basic reagent is sodium carbonate, which has the same desirable properties as caustic soda. However, because it is not so strongly basic, it forms basic salts less readily and is for that reason much more selective than caustic soda. A more unusual, much more selective and yet better-known basic leaching agent is sodium cyanide which, in an oxidizing solution, dissolves gold, silver, copper and a few other metals.

Another important basic solvent is ammonia, which in the presence of anions such as sulphate, carbonate, nitrate or

chloride forms, with certain metals, cationic amine complexes. Because the number of metals that will form amine complexes is small - copper, cobalt, nickel, zinc, cadmium, magnesium, ferrous iron, mercury, palladium, silver, etc. - ammonia is a selective reagent. It is more costly, more volatile and less stable than caustic soda or sodium carbonate, but can be very easily regenerated and has the advantage that, for example, the ammonium sulphate formed in oxidative leaching of sulphides with ammonia is itself a valuable by-product.

All of the above-mentioned leaching reagents are discussed (toxicity, chemical characteristics, environmental effects etc.) in detail in my 244-page report entitled "Use, Characteristics and Toxicity of Mine-Mill Reagents in Ontario". This report is available free-of-charge from the Ontario Ministry of the Environment.

Generally speaking, there are four principal leaching techniques used to recover metals from ore. These are:

(1) dump leaching

(2) heap leaching

(3) in place (in situ) leaching and

(4) vat leaching.

In Ontario, attempts to recover metals by dump or heap leaching of ore are almost unknown. In situ leaching is used on a small scale. Operations that can be related to hydrometallurgical vat leaching are used on a rather important scale.

Before discussing vat-leaching operations, several points must be made:

(1) Commercial leaching operations around the world tend to be largely confined to

(a) oxide ores or mixed oxide-sulphide ores, and

(b) low grade ores which do not easily respond to conventional mine-mill technology.

Oxide ores (copper, lead, zinc, nickel) are not unknown in Ontario but they are rare. Most Ontario ores (copper, lead, zinc, nickel) occur as massive and/or disseminated sulphides in a silicate groundmass. Since the present state of froth flotation technology is somewhat acceptable, it is unlikely that the hydrometallurgical leaching of sulphide ores will assume any great immediate importance in Ontario. On the other hand, hydrometallurgical processes that are based on the leaching of prepared and finely divided mineral concentrates will, in all probability, result in the elimination of the conventional smelter as we know it. Sulphuric acid leaching of raw copper ores has been attempted on a small scale in Ontario.

(2) leaching rates tend to increase with increases of pressure and/or temperature. It is, however, expensive and difficult to run most leaching processes at elevated temperatures and pressures. The ideal leaching process therefore would be one that could produce a commercial leaching rate at atmospheric temperatures and pressures. Since a drop in temperature generally results in a drop in the rate of leaching, winter operations in Ontario will pose problems. Either the slower leaching rate will have to be tolerated or

heat (an operating expense) will have to be introduced into the circuit.

(3) leaching, a chemical reaction, is highly dependent on the available surface area of the substance being leached. In other words, in many cases leaching of ore will not result in high recoveries unless the ore is very finely divided. This is especially true of low grade ores.

All uranium ore in the Province of Ontario is presently being treated using a form of (continuous) vat leaching. Briefly, the uranium (oxide) ore is ground to 65% minus 200 mesh and then introduced (in the form of a slurry) into a series of reactors where the leaching process takes place. Dilute sulphuric acid (75 to 80 pounds per ton ore) is used to leach some of the values from the ore but the extraction is low and an oxidizing agent is required to improve recovery. Air, blown through the mass has become the primary agent of oxidation. A constant temperature of approximately 170^{o} F is attained by sparging raw steam into the pulp. A residence time of 40 to 50 hours is achieved by forcing series operation of the leach-reactors. When leaching has been completed, the waste solids are separated from the uranium-bearing solution and are discarded.

The uranium is recovered as a yellow solid, $(NH_4)_2U_2O_7$, via a series of steps that include filtration, precipitation, and ion-exchange. Massive quantities of many chemicals (80 lbs./ton sulphuric acid, 4 lbs./ton nitric acid, 50 lbs./ton lime, 2 tons/day ammonia etc) are used at each mill. As a result, each mill generates approximately 1,000,000 gallons or more per day of highly contaminated wastewater. Unfortunately, acid mine drainage conditions also exist at the uranium properties. These two wastes together (both carry radioactive substances) act to form one of the most difficult mining waste treatment problems in the Province. The total use of hydrometallurgy in these plants has not resulted in the elimination of environmental pollution. However, if these plants could be put on total wastewater recycle and if gangue sulphide recovery was practiced, the plants would have a minimal impact on the environment. Even at present, the elimination of specific toxic reagents (example: ammonia) from the circuits would result in an improvement relative to the present wastewater flows.

Gold operations in Ontario also rely heavily on hydrometallurgy. Like uranium ore, the gold ore must be finely ground. Although the ore may be first subjected to processes such as mercury amalgamation, roasting and flotation, it eventually ends up in intimate contact with a cyanide leach-solution. The cyanide forces any available gold into solution. The gold is recovered by precipitation. Depending on the type of gold circuit, reagents such as lime, sodium cyanide, zinc dust, lead acetate, lead oxide, mercury and many common flotation chemicals find use. The waste flows from the gold mills strongly reflect the reagents used. Cyanide and sometimes soluble arsenic characterize these flows. Both the uranium and the gold hydrometallurgical processes create major tailings disposal problems.

HYDROMETALLURGICAL vs. PYROMETALLURGICAL EXTRACTION

Most of the world's base metals are extracted from their ores and concentrates by pyrometallurgical treatment. This process traditionally includes three sequential operations: roasting, smelting, and converting. The operations are briefly summarized as follows:

1. Roasting: Sulphur is driven off as sulphur dioxide with minor amounts of other sulphur oxides and the iron is oxidized. This step is only necessary when excessive amounts of sulphur are present.
2. Smelting: The roaster product is melted with a siliceous flux that combines with the gangue minerals to form a molten silicate slag and a solution of molten sulphides.
3. Converting: The remaining sulphur is driven off and the remaining iron is oxidized and fluxed for removal as a silicate slag.

Roasting

Roasting is a process where sulphide concentrate containing an above average sulphur content is heated in air (which may be enriched with oxygen) to a temperature at which oxygen combines with the sulphur to form sulphur dioxide and with the metal to form metallic oxides. The amount of sulphur removed is regulated by the amount of oxygen and the furnace temperature. This must be controlled because sufficient sulphur must remain to produce the desired grade of matte.

There are three types of roasters. The multi-hearth roaster is the oldest. Due to the relatively long time required in roasting, it has largely been replaced by fluid bed roasters. The third type, the sintering machine roaster, is used to agglomerate the concentrate for smelting in a blast furnace. Figure 1 shows a cutaway view of a fluid bed roaster.

Smelting

Ores and concentrates are smelted either in blast furnaces or reverberatory furnaces. In the blast furnace, the ore is mixed with the fuel and burned by blowing air through the mass. Traditionally, this type of furnace was used for massive sulphide lump ore. Flotation concentrates replaced direct smelting ores as the rich deposits became exhausted. To be used in the blast furnace, these concentrates must be agglomerated to eliminate excessive dust losses. In reverberatory smelting, the ore and fuel are kept separate, and the ore is melted by hot gases which pass over it. With this furnace, fine concentrates can be used as feed without sintering. Consequently, the reverberatory furnace has largely replaced the blast furnace.

Today, because of air pollution control problems with the reverberatory furnace, the blast furnace is being reconsidered.

Most ores are difficult to fuse alone and do not

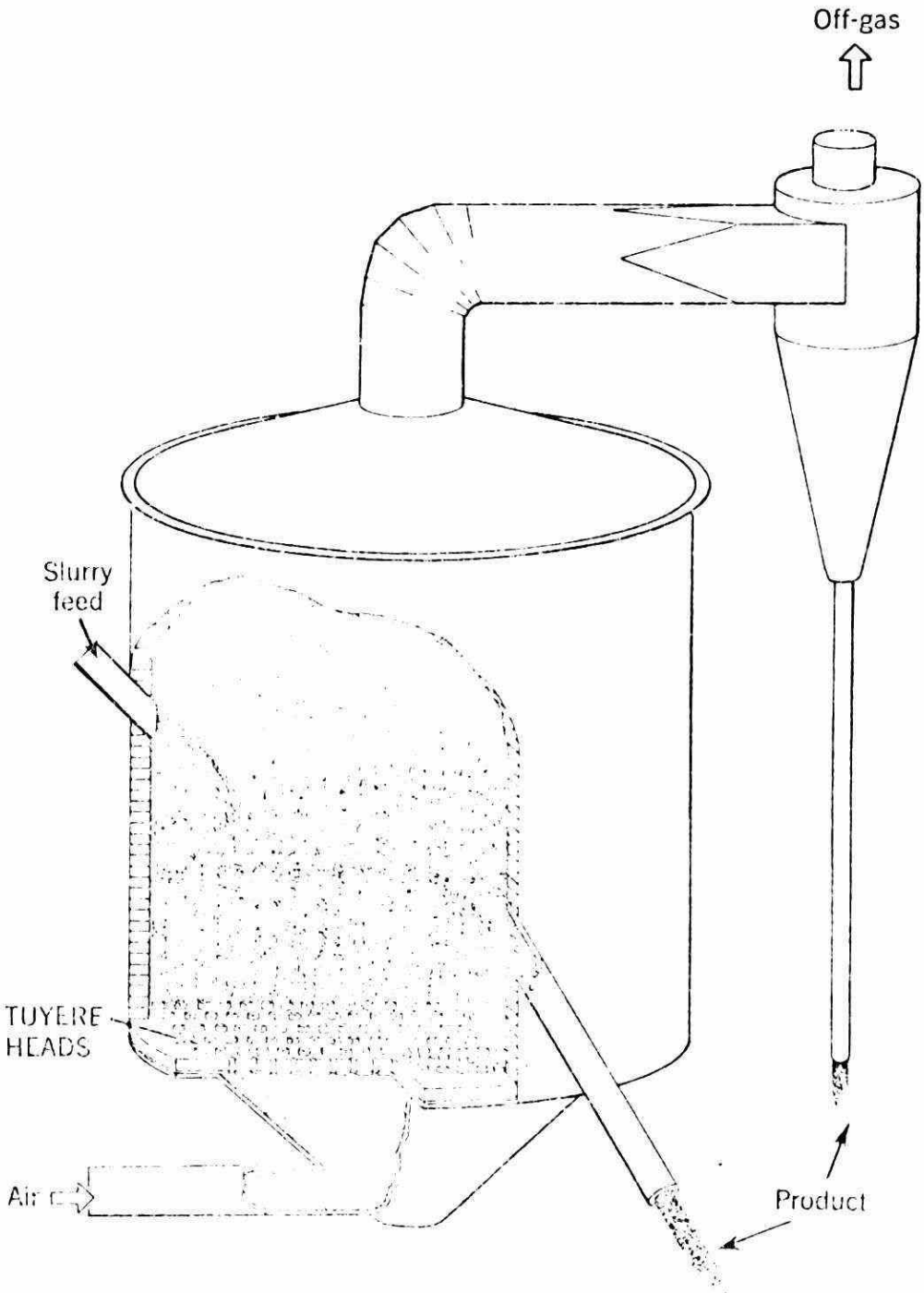


Figure 1 Cutaway View of a Fluid Bed Roaster

develop sufficiently fluid slag to allow quick, thorough, sulphide concentration. For this reason, a flux is usually added. If the ore is basic, an acid flux, such as silica, is added. If the ore is acid, a basic flux, such as limestone, is added. The three elements of the charge are then proportioned (fuel, flux, and concentrate), so as to obtain the highest metal concentration with the least amount of fuel and flux.

Reverberatory furnaces are used to produce matte. Matte is defined as a complex artificial metallic sulphide. The main constituents are sulphur, copper, iron, lead, nickel, and small amounts of some additional secondary metals. The residual or remaining slag contains the valueless constituents of the ore and is drawn off the top of the molten bath. Not all of the sulphur remains in the matte. A portion of it passes into the flue as sulphur dioxide gas and a small portion of this is converted to sulphur trioxide.

At the high temperature of a smelting furnace, copper, nickel, and other precious metals have an affinity for sulphur. Therefore, these metals will combine with enough sulphur to convert all the copper and nickel to sulphides. Any sulphur remaining will combine with other metals, particularly iron, or be lost to the atmosphere. If there is a large excess of sulphur in the ore, then some

will be roasted off prior to smelting. This helps to eliminate dilution of the matte by large quantities of iron sulphide. If the matte is made too rich, some of the copper will be lost. Generally, a matte of 45% to 60% metal is sought.

Reverberatory furnaces (Figure 2) that treat unroasted concentrates produce a steady flow of gases having a very low concentration of SO_2. This concentration can be less than 1% of the total gas volume. Acid plant technology requires a minimum of 4% SO_2 concentration in the offgases for sulphuric acid manufacture. Recovery of the low SO_2 concentrations produced in the reverberatory furnace is at this time unfeasible both technically and economically by available processes.

The operation of the reverberatory furnace is a batch process and thus only one or two charges of ore are treated at a time. The chemical reactions that occur are as follows:

$$9\ NiO + 7\ FeS \longrightarrow 7\ FeO + 3\ Ni_3S_2 + SO_2$$

$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

As mentioned earlier, hot air and gases are blown across the top of the charge and thus fine material can be treated effectively. The charge must be agitated to ensure good fusion.

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4. Accurate location of mine-mill complex:

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NOTE: If the mine or plant is situated in unsurveyed lands, attach a location plan that shows the surveyed latitude and longitude of the mine shaft or plant together with its position relative to the surface property of the mine or plant and its position relative to identifiable physical features in the vicinity.

5. Attach a simple layout plan showing the relative locations of the mine, mill and tailings area. Please include gas, electricity, and water utility route locations and also road and rail access to the mine or plant. If unusual transportation difficulties are encountered, please explain.

6. Indicate the total extent (in acres) of Company held ground. Also indicate the number of claims held and the official serial numbers of the individual claims:

Total Area ..... acres

M I N E R A L I N D U S T R I E S

INFORMATION SHEET

NOTE: This "Information Sheet" is used by the Ontario Ministry of the Environment as an aid in the environmental evaluation of new mining properties.

Part I

GENERAL

1. Name of Applicant: .....
(company, corporation, owner)

....
(Tel. number) (postal address)

2. Officers of Company:

(a) ....
(President) (Tel. number)

.....
(postal address)

(b) ....
(Mine Manager) (Tel. number)

.....
(postal address)

(c) ....
(Mill Manager) (Tel. number)

.....
(postal address)

3. Briefly describe the proposal.

.....

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A major factor in the process's viability is the disposal of byproduct sulphate. The sulphate discard can be treated with lime and heated to drive off ammonia, yielding gypsum: or, ammonium sulphate can be recovered.

Pilot-plant operations to date have shown copper recoveries in the range of 97 to 99%: lower recoveries may be deliberately sought in actual practice, with residual values in copper and precious metals extracted by other means.

Both of the above processes as well as most others work with a feed of mineral concentrate. As such, the waste disposal problems that are encountered during conventional mining and milling will remain as they are. Only the smelter and perhaps the refinery will be affected. The sulphur dioxide and smoke plumes will be gone. The airborne suspended matter will be gone. In their place we will have different problems; mostly associated with water pollution and perhaps of a minor nature.

From an environmental standpoint, hydrometallurgy is the route to follow. We will have to find suitable disposal sites for leach residue and we will have to contend with such things as plant bleed-off and accidental rupture of solution storage tanks etc.

The electrolytic iron recovered is of very high purity.

In summary, the Cymet process reduces hazards of pollution because the major waste product is the tailings that can be impounded in the normal manner. Various minor discharges can be easily neutralized, and dust problems in the feed section can be controlled by normal equipment.

(2) The ARBITER Process

This process is essentially an ammonia leach using oxygen but requiring no pressure or elevated temperatures as do several similar processes under development. Equipment costs are thus a fraction those of a pressure leaching process and plant costs are estimated to be about half those of a conventional smelter.

The process is straightforward with slurried concentrate leached with ammonia in rubber-lined tanks. Leached products are decanted and countercurrently washed, with the pregnant solution being filtered and copper extracted from it with an organic solvent.

The copper is stripped from the organic by means of an acid electrolyte, and recovered by electrowinning. It was first thought that melting and refining of the copper cathodes thus obtained would be required, but by adding some cobalt to the electrolyte, a purity problem with lead was solved and the copper is as good as electrolytic copper.

The chemical reaction:

$$3CuCl + 3e \longrightarrow 3Cu^{\circ} + 3Cl^{-}$$

The copper powder eventually goes to electro-refining.

Two other major products are recovered in the Cymet process. The underflow from the first thickener is filtered and the solids washed, then reslurried and transferred to an autoclave where heat (135 to 140 C) and agitation are applied for two hours. Sulphur globules thus formed are solidified into beads by controlled cooling and screened off. Screen underflow is subjected to flotation, with tailings rejected and concentrates recycled to the leaching operation. Oxidizing sulphide sulphur to elemental sulphur rather than to sulphate sulphur requires considerably less electrical power input.

Before iron is recovered from the overflow from the copper electrolysis thickener, impurities are removed by precipitating them first with iron powder and then zinc powder. The electrolysis that follows serves a double purpose - it regenerates the remaining ferrous chloride to ferric chloride for recycle, and it removes most of the iron. These are the reactions:

$$3FeCl_2 + 6e \longrightarrow 3Fe^{\circ} - 6Cl^{-} \text{ (cathode)}$$
$$6FeCl_2 + 6Cl^{-} \longrightarrow 6FeCl_3 \text{ (anode)}.$$

Countercurrent leaching employs cyclones between leaching stages to provide maximum efficiency.

Leached slurry goes to the anode compartment of electrolytic dissolution cells, which are diaphragm-fitted cells with a woven permeable synthetic material that separates anode from cathode compartments. Anodes are titanium, coated with conducting oxides.

The chemical reaction at the anode is:

$$CuFeS_2 + 3HCl - 3e \rightarrow CuCl + FeCl_2 + 2S + 3H+.$$

Slurry discharge from this compartment is recycled to the final leach stage in countercurrent flow.

Copper is recovered from the leach and anolytic solutions by electrowinning in the cathode compartments of the cell. The catholyte solution comes largely from the hydroclone overflow product from the leaching step: this stream goes to a thickener for further liquid-solid separation. Then the overflow goes through a polishing filter to remove any remaining solids prior to electro-precipitation of copper, etc., in the cell. Cathodes are round copper rods, uniformly spaced and oriented parallel to anodes in the opposite compartment. Metals are precipitated as elemental powders, which are removed in slurry and thickened prior to filtration.

In comparison, there are many pure hydrometallurgical processes available that could, if the economics are right, replace conventional smelter routes. The two well-known hydrometallurgical routes are:

(1) The Cymet Process and

(2) The Arbiter Process.

The following is a very brief description of each:

(1) The CYMET Process

The Cymet process is considered virtually pollution-free. Water is processed and reused and all sulphur is captured and recovered in elemental form, easy to store and transport.

Other advantages claimed:

- Costs comparable to pyrometallurgical smelting, with advantages anticipated as equipment and techniques are improved.
- Lower capital investment, smaller plants feasible.
- Reduced energy costs, based on electricity rather than natural gas.
- Flexibility in handling various feedstocks.

In general, sulphide concentrates are ground in ball mills to a fineness of at least 95% minus 200 mesh, to facilitate contact in the leaching step. Leaching with ferric chloride anolyte solution from the iron electrolytic cells produces the following reaction:

$$6FeCl_3 + 2CuFeS_2 \rightarrow 2CuCl + 8FeCl_2 + 4S.$$

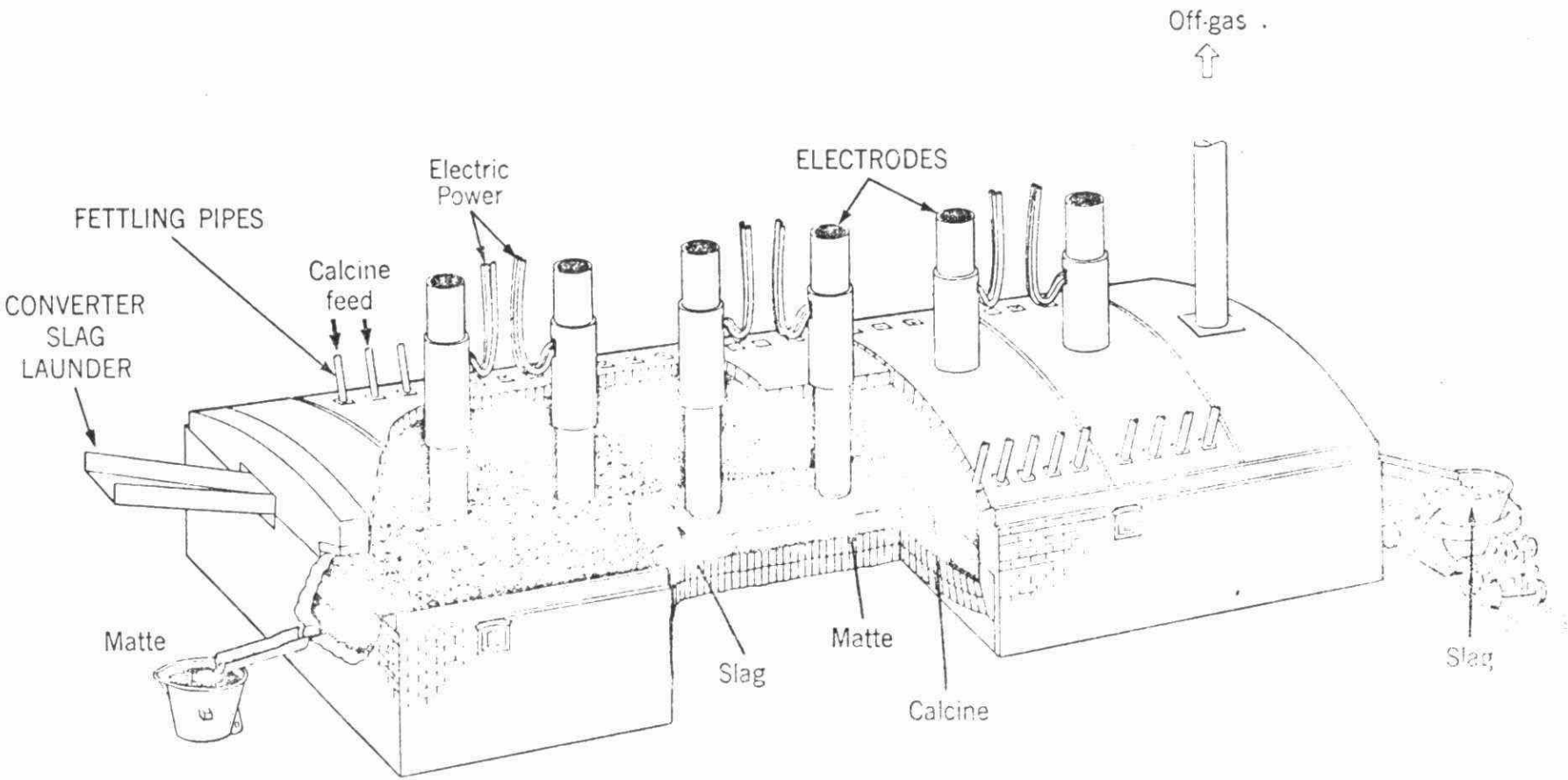

Figure 9 Cutaway View of a Submerged Arc Electric Furnace

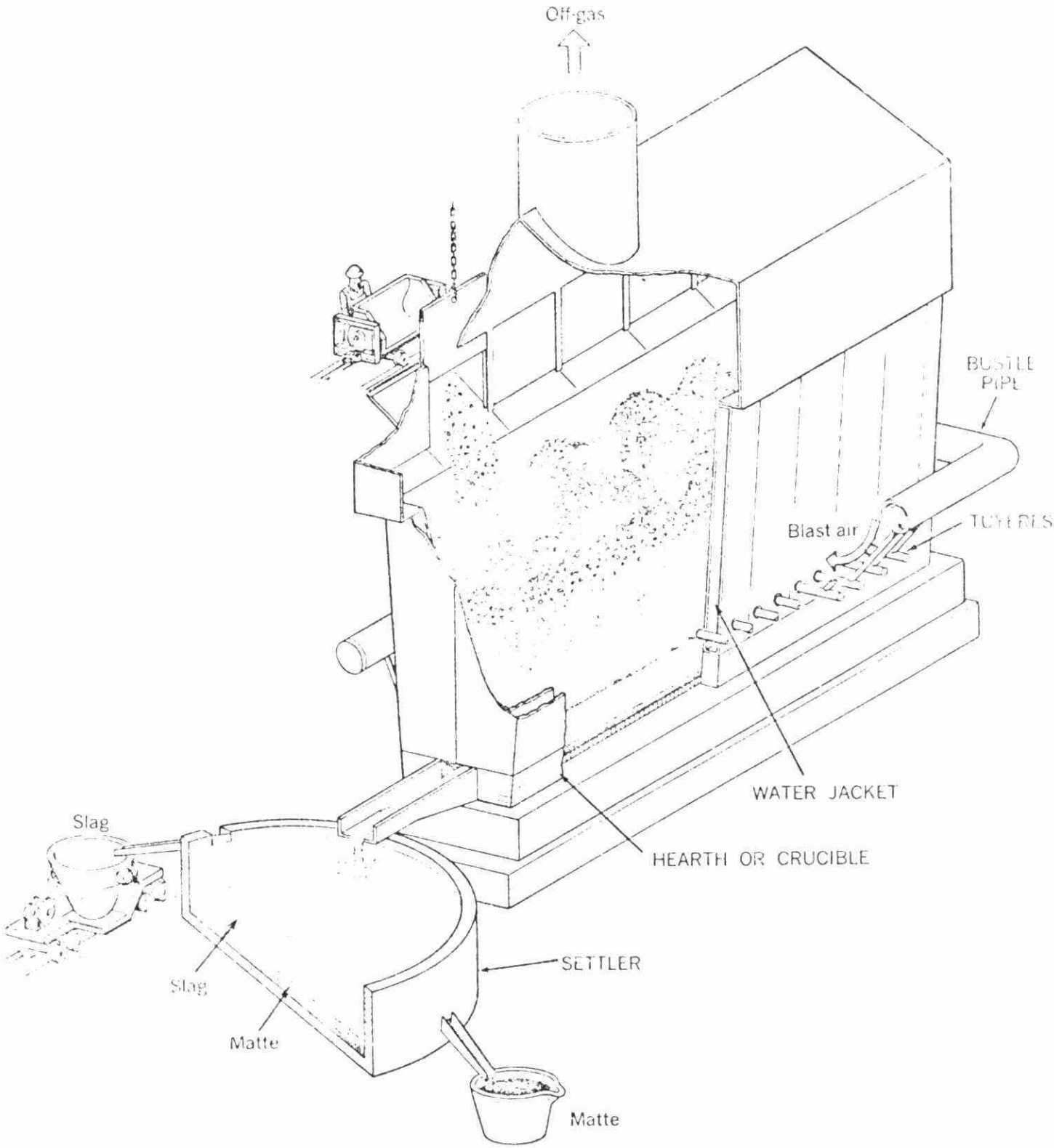

Figure 8 Cutaway View of a Blast Furnace for Sulfide Nickel Ore

Blast Furnace Smelting

The blast furnace is a vertical shaft type furnace and may be used to produce either matte or blister copper. Matte is most commonly produced. Figure 8 shows a cutaway view of a blast furnace used to smelt nickel sulphide ore. The ore is mixed with the fuel and burned by blowing air through the mass.

This system combines roasting and reverberatory steps and occasionally when blister copper is produced, the converting step is also included. The main problem with blast furnace smelting is the excessive dust produced when air is blown through the mass. The ore must be either lump ore or sintered concentrates, with no fines present, if the furnace is to work effectively.

Electric Arc Furnace

Electric furnaces are sometimes used when electricity is cheap or when required smelting temperatures are very high. Figure 9 shows a cutaway view of a submerged arc electric furnace. Since there is no fuel combustion, the quantity of exit gas is greatly reduced. This produces higher SO_2 concentrations and easier heat and dust recovery. The electric furnace produces a matte, meaning the converter is still necessary to produce blister copper.

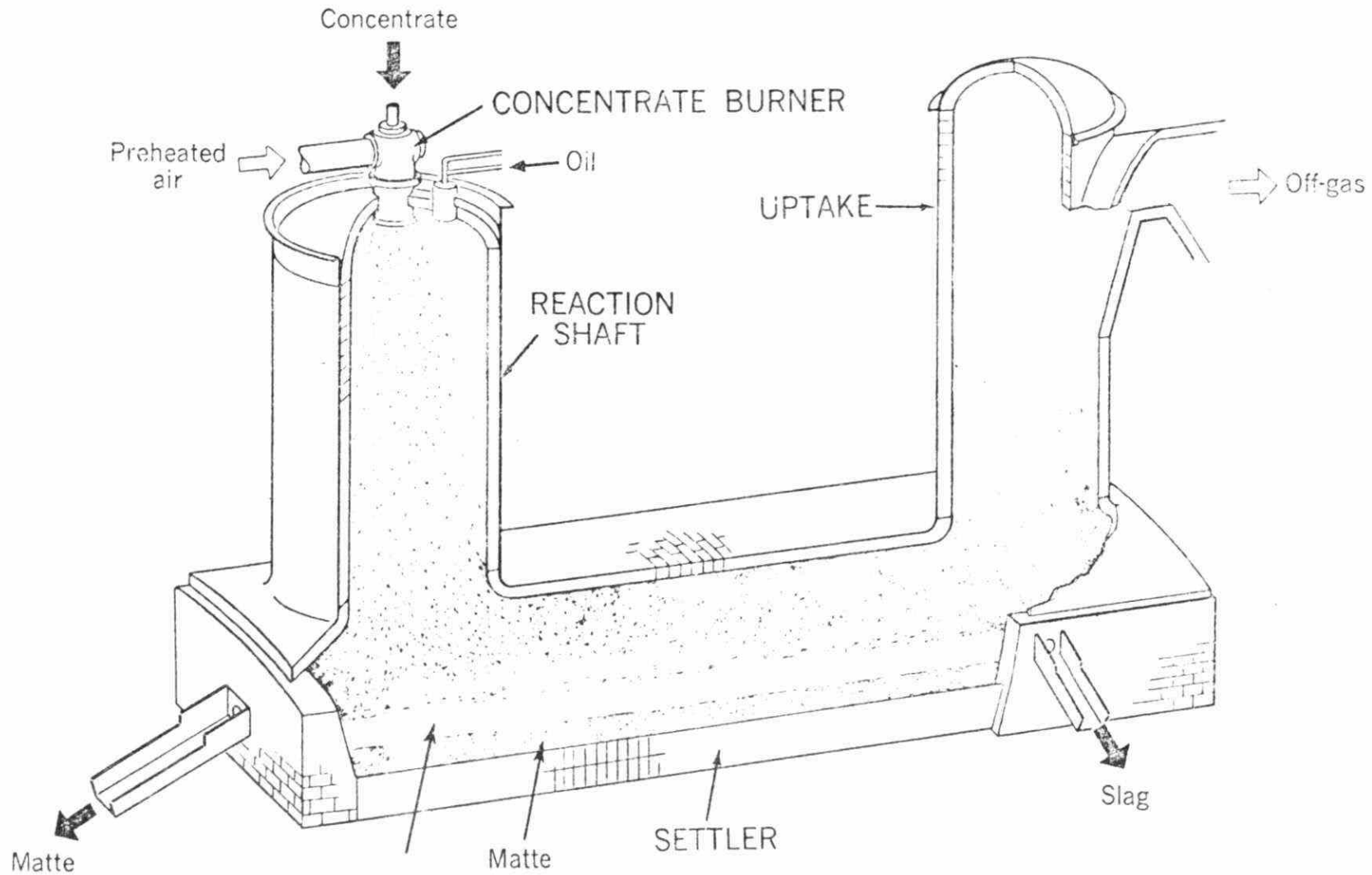

Figure 7 Cutaway View of Outokumpu Flash Smelting Furnace

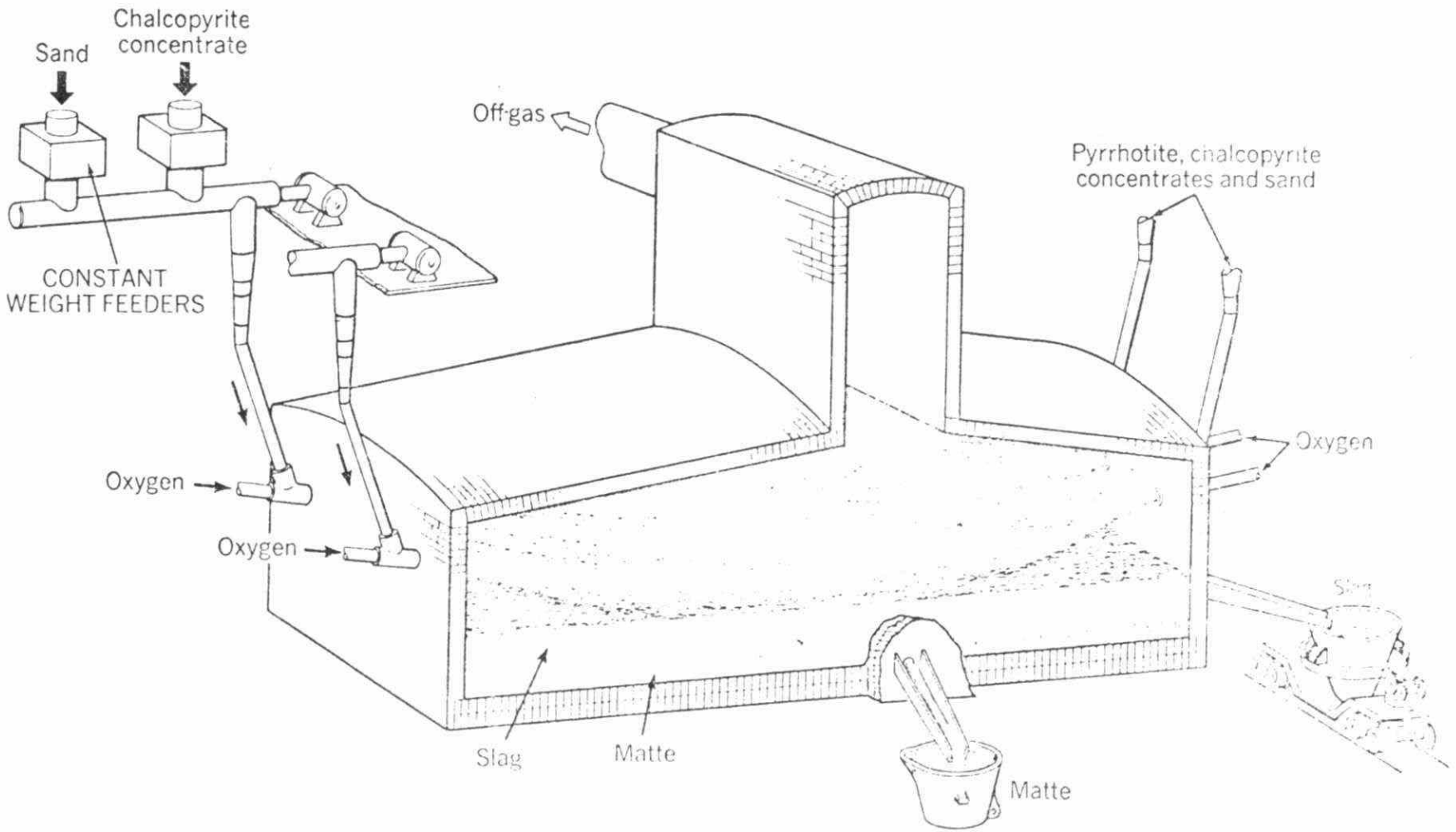

Figure 6 Cutaway View of INCO Oxygen Flash Smelting Furnace

cleaned for waste heat utilization and production of sulphuric acid; or because of low oxygen content, the gases can be used to produce elemental sulphur.

These processes have been successfully operated in pilot plants and commercial plants are under construction but as yet are untried on a commercial scale.

Flash Smelting

This process combines into a single operation, conventional roasting and smelting steps. The converting process remains the same as in traditional smelting. A sulphide concentrate is flash smelted by burning some of its sulphur and iron content while suspended in an oxidizing medium. The grade of the matte is controlled by regulating the ratio of oxygen to sulphur in the feed. Flash smelting combines two operations, and will hopefully permit economical treatment of flash furnace gases. The offgases from the converter are the same as those produced in conventional converting.

The flash smelter was developed after World War II and has been successfully operated in several commercial size plants using both copper and nickel concentrates as feed material. Figures 6 and 7 shows a cutaway view of two commercial flash smelters. Magma Copper Company recently announced plans to construct a flash smelter in Arizona as part of their pollution control program.

1. Concentrates and feed are introduced in one end of the reactor which is similar in cross-section to a Pierce-Smith converter.
2. Smelting takes place at the feed end.
3. Matte and slag flows are controlled as they move slowly to tapping ports.
4. Oxidizing gas is introduced into the matte to oxidize the FeS.
5. Continued injection of the gas into the resulting white metal gradually oxidizes the Cu_2S to metallic copper.
6. Metallic copper is tapped periodically after settling periods.

The WORCRA process is outlined as follows:

1. Metal is produced directly from concentrates in one unit.
2. Most of the exothermic oxidation reactions are generated and continue in the liquid bath.
3. Turbulence is generated in the smelting and converting zones by lance-injected oxygen-containing gas.
4. Slag moves countercurrent to matte and metal flow in the converting zone.
5. Copper-in-Slag is reduced to throw-away levels. There is no 'revert slag'.
6. SO_2-bearing gases of rich tenor exit through a single offtake. Furnace gases rich in SO_2 can be cooled and

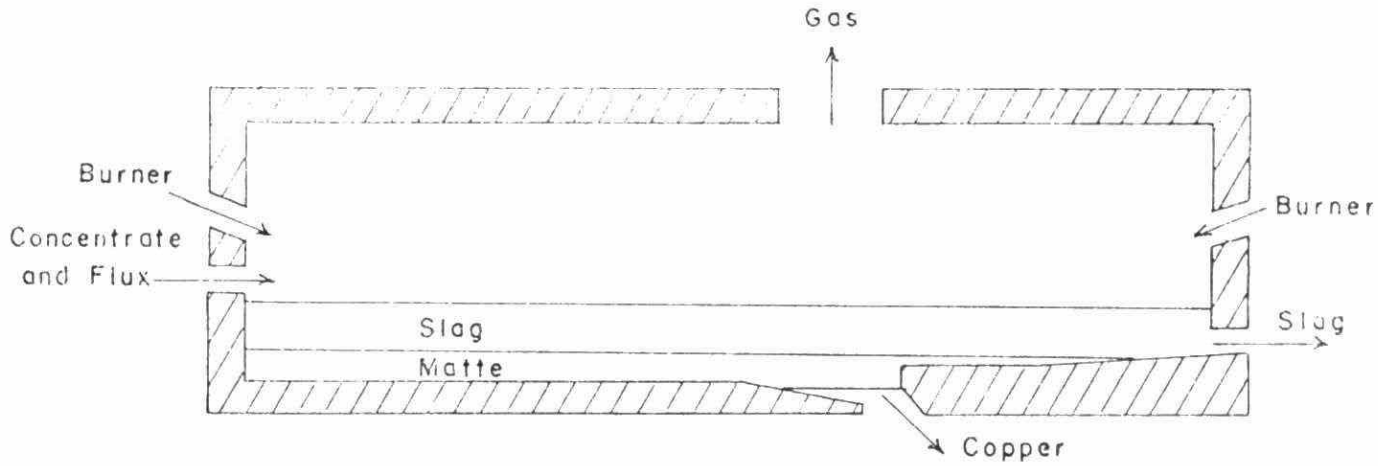

Figure 4. Noranda Continuous Smelting Furnace

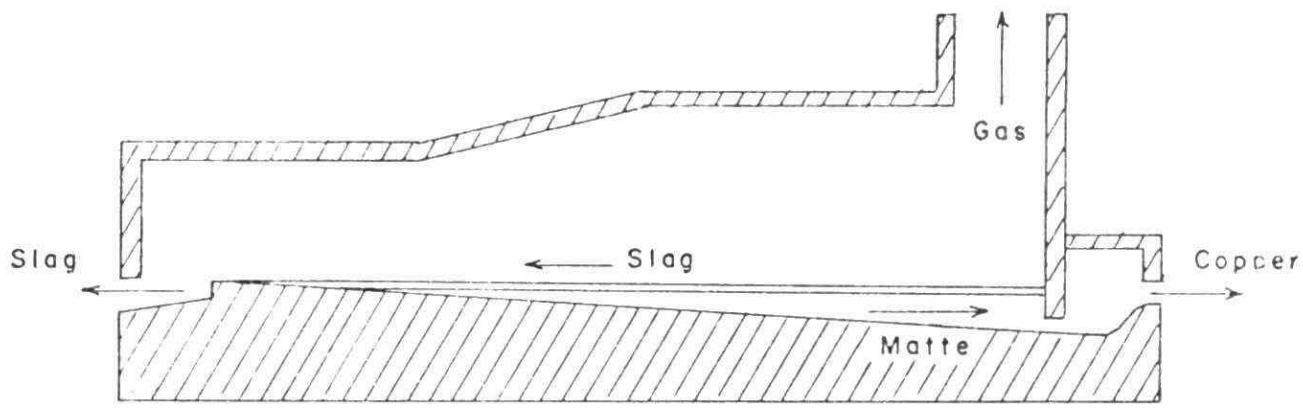

Figure 5. WORCRA Continuous Furnace

3. Smelting operations should use less total fuel. More heat should be recovered and emphasis should be on heat utilization.
4. All useful materials should be recovered from the initial feed material. Waste products which are produced should be non-polluting and in a form which can be disposed of readily.

Four systems which are being considered to replace conventional methods are:

1. Continuous Smelting
2. Flash Smelting
3. Blast Furnace Smelting
4. Electric Furnace Smelting.

Continuous Smelting

Two continuous smelting processes are being considered to replace conventional smelting. Noranda Mines Ltd., recently announced plans to build a $19 million commercial prototype of the Noranda continuous furnace shown in Figure 4. In Australia, the WORCRA process has been developed and the WORCRA continuous furnace is shown in Figure 5 . Both methods combine conventional roasting, smelting, and converting steps into a single step. This results in higher concentrations of SO_2 that presumably can be recovered economically. The Noranda process is outlined as follows:

In some cases, fusion techniques may also be used. For example, refractory minerals of tantalum and columbium are usually insoluble even in the strongest acid or alkaline solutions. It is common practice to fuse these minerals in molten caustic (NaOH) or sodium bisulphate ($NaHSO_4$), thus converting the metals to the corresponding sodium salts (sodium tantalate, columbate, etc.) which can then be dissolved in aqueous solutions, separated and recovered.

By no means do we assume that pure hydrometallurgical routes will replace the conventional smelter. We only assume that this is probable. There is always the chance that new pyrometallurgical processes can replace existing pyrometallurgical processes and, at the same time, solve outstanding pollution problems.

Because of the air pollution problems associated with the conventional extraction methods, several alternate methods have been suggested as possible replacements. Such systems attempt to incorporate the following features:

1. Smelter systems should produce SO_2 in higher concentrations and in uniform volumes. This can probably be done by replacing batch processes with continuous processes and by combining extraction steps.
2. Gas cleaning systems should be more efficient and reliable and capable of operating at high temperatures.

the vanadium, normally insoluble after roasting, can be rendered soluble by roasting with the admixture of calcium sulphate or salt which converts the vanadium to a soluble vanadate. In the sulphuric acid "bake" (commonly used in preparing ores, flue dusts and similar materials containing copper, cobalt, germanium and other metals for subsequent leaching) the ore is mixed with concentrated H_2SO_4 and baked at relatively low temperatures to produce soluble sulphates of the metals.

3. Nonoxidizing Roast - Minerals such as pyrite and arsenopyrite when heated to a suitable temperature without access of air are decomposed, the "free" atoms of sulphur and arsenic being volatilized, leaving a residue which resembles pyrrhotite ($Fe_{1-n}S$). In this form they react with solutions of ferric chloride, chlorine, oxygen or other strong oxidizing agents to produce elemental sulphur.

4. Reducing Roast - The purpose of the reducing roast is to reduce selectively metal oxides to metallic form. Nickel silicate ores, for example, containing magnesia, silica and iron oxide, as well as nickel and cobalt in oxidized form are heated in the presence of reducing gases (H_2 and CO) under such conditions that only nickel and cobalt are reduced to metallic form, the iron, silica and magnesia remaining as oxides. The metallic nickel and cobalt can then be selectively dissolved in oxidizing solutions containing ammonia and ammonium salts.

roasted in air to convert the dense sulphide minerals to porous oxides, thus permitting access of cyanide leaching solution to gold particles which were originally occluded by the sulphides.

By proper control of temperature and gas concentration, cobalt and iron sulphide ore, for example, can be roasted to convert the cobalt sulphide to cobalt sulphate and the iron sulphide to iron oxide, thus giving a product from which the cobalt sulphate can be extracted with weak sulphuric acid leaving an insoluble iron oxide residue.

2. Oxidizing Roast With Added Reagents - The object of this procedure is to convert some of the metal compounds in an ore to soluble form, leaving others as insoluble compounds. Thus, residues from pyrite burning which contain small amounts of copper, cobalt, nickel, zinc, gold, silver and other valuable metals are mixed with salt (NaCl) and roasted to convert the valuable metals to soluble chlorides, leaving the iron as an insoluble oxide. Similarly, nickel oxide containing 0.1% sulphur is mixed with a small amount of soda ash (Na_2CO_3) and roasted at 1,200° C: the soda ash reacts with the sulphur to form sodium sulphate (Na_2SO_4) which can be dissolved with water, leaving sulphur-free nickel oxide.

Also, with ores containing both uranium and vanadium

the smelter route can be completely avoided. This is where hydrometallurgy will play its biggest and most important role in the future. Using hydrometallurgical technology, metals can be recovered from their respective sulphides. No sulphur dioxide is produced and extremely high temperatures are not needed. However, as I have indicated throughout this paper, hydrometallurgy is not entirely a pollution-free route. We will be replacing major air pollution problems with (hopefully) minor water pollution problems. However, adequate technology for the treatment of such wastewater is now available.

I would like to add one note of caution. A new smelter-like plant may be publicized as being hydrometallurgical in character. This does not necessarily mean, however, that sulphur oxide emissions have been eliminated. Many sulphide ores are roasted before being leached. The roasting drives off sulphur as sulphur oxide. Examples of the various types of roasts are as follows:

1. Oxidizing Roast - Sulphide ores of zinc, copper, cobalt and some other metals are oxidized in air at temperatures above 500° C to produce the metal sulphates or oxides which, unlike the sulphides, are readily soluble in weak sulphuric acid. Ores containing gold in the presence of sulphides such as pyrite (FeS_2) or arsenopyrite (FeAsS) are

As we all know, the treatment of sulphide concentrates in conventional smelters has given rise to very serious pollution problems in many parts of the world. Ontario is no exception. Although some water pollution does occur, air pollution is the main concern. The two main air pollution problems that are associated with the traditional pyrometallurgical approach to base metal extraction are: (a) excessive dust, and

(b) sulphur oxide emissions.

Dust recovery technology is sufficiently advanced so that finely divided suspended material can be recovered from a waste gas stream. The recovery of a satisfactory amount of sulphur dioxide, however, is a problem of some magnitude. Some smelters operate in conjunction with a sulphuric acid plant; - that is a plant that recovers sulphur oxides from a waste gas stream and uses them for the production of sulphuric acid. The trouble is, in order to be efficient, these plants need to operate on a waste gas stream that is steady in volume and relatively rich in sulphur dioxide. Not all waste gas streams produced by smelters have these specifications. The acid plants, of course, produce great quantities of sulphuric acid for which a market may or may not be found.

Some hydrometallurgical processes are such that

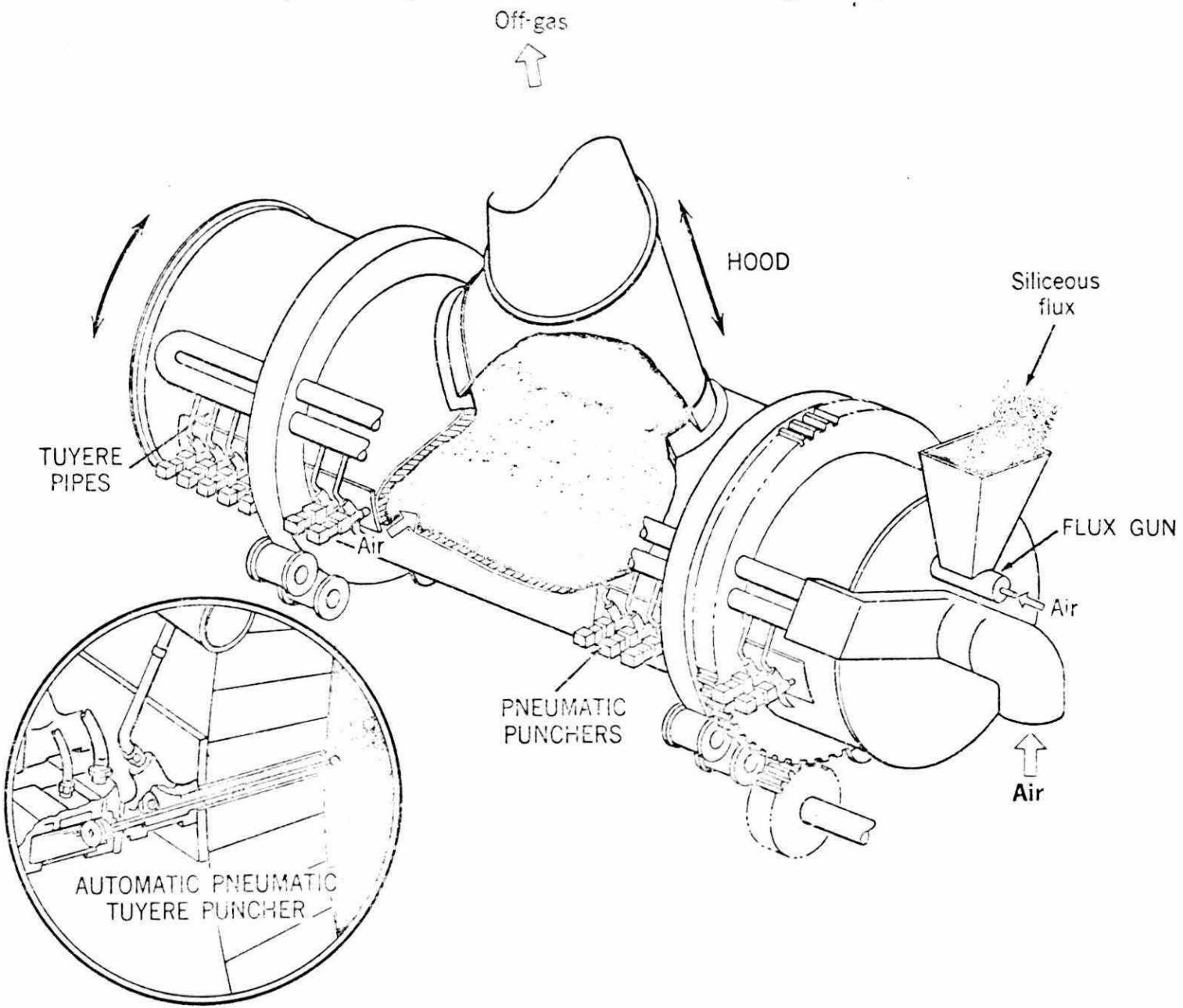

Figure 3 Cutaway View of a Horizontal Side-blown Converter

Converting

A major objective is achieved in the reverberatory furnace: all of the rock and most of the iron is removed. The matte is a complex homogeneous melt containing nickel, copper, iron, and sulphur, plus small amounts of other base elements. The converting process consists of oxidizing the sulphur and iron by blowing a strong blast of air through the molten matte. This produces metallic copper, nickel, and other precious metals. The heat generated keeps the charge fluid. The sulphur is driven off as sulphur dioxide, and the ferrous oxide combines with a silica flux to form a slag. Converting is also a batch process and produces intermittent quantities of high concentrations of SO_2 gases. Figure 3 shows a cutaway view of a side blown converter.

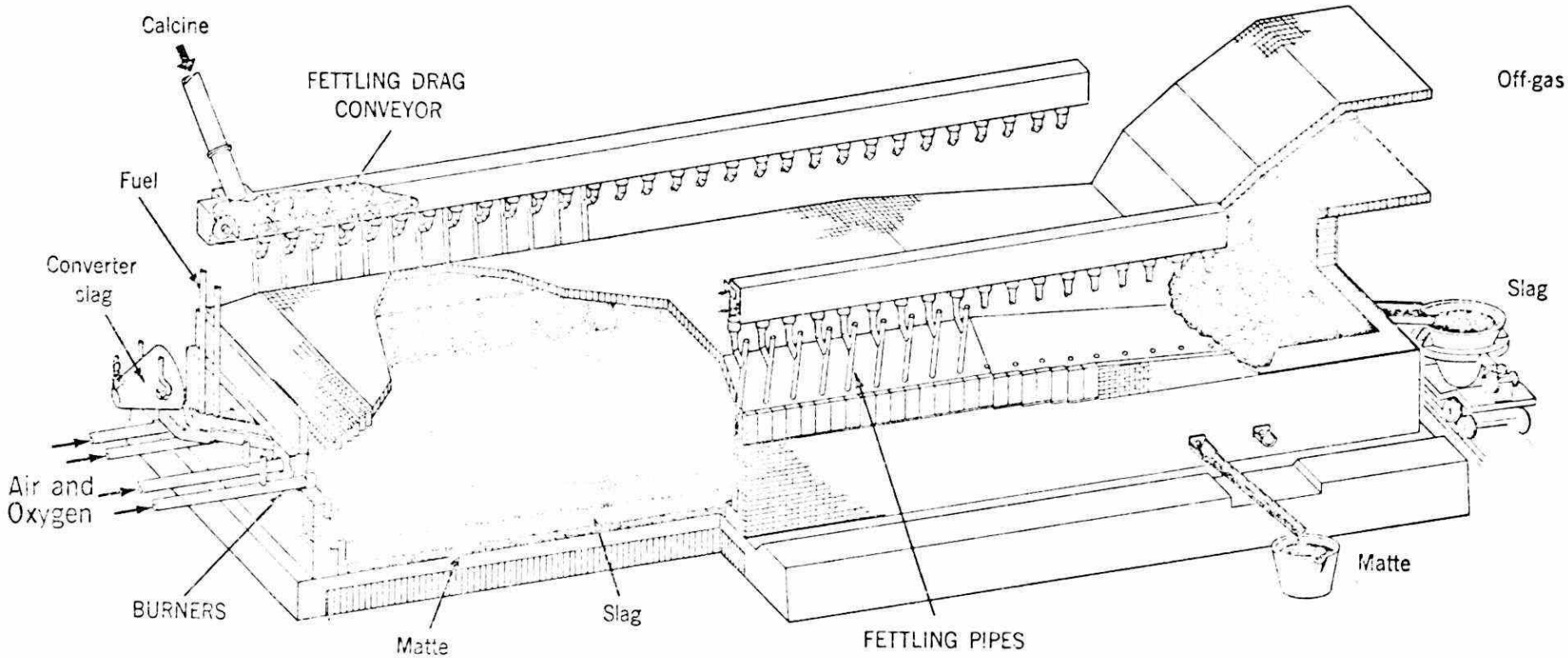

Figure 2 Cutaway View of INCO Reverberatory Furnace

Total Number of Claims .....

Claim Serial Numbers:

....

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7. If the property is not yet in operation, indicate the date on which the mine and/or mill will commence production:

Mine ..... Mill .....

In Operation ..... In Operation .....

8. Indicate the status of the mine and/or mill on the date of application:

	Mine	Mill
Design	.....	.....
Under Construction	.....	.....
Operation	.....	.....
Suspended	.....	.....
Abandoned	.....	.....

9. Indicate the present (or proposed) mine-mill operating schedule:

(a) Mine:		(b) Mill:	
hours per day	.....	hours per day	.....
days per week	.....	days per week	.....
weeks per year	.....	weeks per year	.....
shift periods	.....	shift periods	.....
	.....		.....
	.....		.....
no. of employees	....	no. of employees	...

10. Indicate the type of mining operation to be used on the property:

conventional underground .....

conventional open pit .....

other underground operations (e.g., bacterial leaching) .....

combined open pit and conventional underground .....

strip mining .....

other mining activity (please explain) .....

.....

.....

.....

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.....

11. The Atmospheric Environment:

The applicant should provide an analysis and interpretation of the published meteorological information collected at the most applicable Department of Transport meteorological station where such analysis and interpretation are available. The following parameters should be considered:

(a) wind speed and direction:

(i) average frequency of winds of a given velocity and direction

(b) temperature:

(i) average temperatures on a monthly basis

(c) precipitation

(i) mean monthly precipitation and mean yearly precipitation (expressed in inches)

12. Physiography:

The applicant should provide an analysis and interpretation of the geologic and hydrologic environment within a circle of 5 miles (more or less) radius centered at the mine or plant based on existing information and such new information as may be required. The investigation should extend from ground surface downward to the base of the glacial drift. The Applicant should provide:

(i) topographic maps: copies of the most recent and largest scale topographic maps available covering the area where the mine, mill, and waste disposal basin are (or are to be) located.

(ii) soil maps: copies of the most recent and largest scale soil maps available covering the area where the mine, mill, and waste disposal basin are (or are to be) located.

(iii) geologic maps: copies of the most recent

geologic maps and reports available that cover the area where the mine, mill, and waste disposal basin are (or are to be) located.

13. Describe accurately but briefly any property development ((shafts, adits, mills (give rated capacity, etc.), tailings areas, etc.)) that took place before the present company gained control of the property:

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14. Were (or will) any old workings (be) dewatered in order to bring the present property into production?

Yes ..... No .....

15. If "yes" above, indicate the total volume of water discharged or to be discharged, and the chemical characteristics of the water discharged or to be discharged.

Total Volume ..... Imperial Gallons

Receiving Watercourse (name of).....

Chemical Characteristics of Discharge:

.....	.....
.....	.....
.....	.....
.....	.....
.....	.....

16. Was (or will) the above discharge (#15) (be) treated chemically?

Yes ..... No .....

17. If "yes" above, describe the applied treatment:

.....

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NOTE: If underground workings, pits, etc., are to be dewatered for any purpose, the resultant water must be acceptable for discharge to a natural watercourse. If the water that is to be pumped, etc., from the workings is impaired in any sense then chemical treatment of the water is required before discharge. Any liquid waste generated during periods of exploration and/or development must be likewise treated before discharge to a natural watercourse.

Part II

GEOLOGY - MINERALOGY

18. Briefly describe the physical nature of the orebody. Please include known dimensions and approximate shape:

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19. Briefly describe the country rock in the general vicinity of the orebody:

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20. List, in order of importance, the ore minerals of the deposit:

	Mineral	%
1.	.....	.....
2.	.....	.....
3.	.....	.....
4.	.....	.....
5.	.....	.....
6.	.....	.....

21. List, in order of importance, the individual gangue minerals that occur within the orebody:

	Mineral	%
1.	.....	.....
2.	.....	.....
3.	.....	.....
4.	.....	.....
5.	.....	.....
6.	.....	.....

22. Are pyrite (marcasite) and/or pyrrhotite present in the orebody?

Yes ..... No .....

23. If "yes" above, please indicate the amount of each

present in the orebody.

pyrite .....% pyrrhotite .....%

pyrite-pyrrhotite mixture .....%

24. Is arsenopyrite present in the orebody?

Yes ..... No .....

25. If "yes" above, please indicate the amount of arsenopyrite present.

.....% arsenopyrite

26. Indicate the <u>average</u> grain size of the ore minerals. Please include pyrite and/or pyrrhotite if present in the orebody.

	Mineral	Mesh No.	Other Size Description
1.	.....	.....	.....
2.	.....	.....	.....
3.	.....	.....	.....
4.	.....	.....	.....
5.	.....	.....	.....

Part III

THE MINE

27. Indicate the number of shafts or other openings that are presently on the property. Please signify whether or not the openings referred to are presently in use:

Shaft (name or number)	Present Depth	Proposed Depth
.....	.....	.....
.....	.....	.....
.....	.....	.....
.....	.....	.....
.....	.....	.....

Adit (name or number)	Present Length	Proposed Length
.....	.....	.....
.....	.....	.....
.....	.....	.....
.....	.....	.....
.....	.....	.....

Open Pit	#1	#2	#3	
Present Surface Length	.....	.....	.....	feet
Maximum Future Surface Length	.....	.....	.....	feet
Present Surface Width	.....	.....	.....	feet
Maximum Future Surface Width	.....	.....	.....	feet
Present Depth	.....	.....	.....	feet
Maximum Future Depth	.....	.....	.....	feet

28. If open pit operations are presently being carried out or are proposed, will conventional underground operations follow?

Yes ..... No .....

29. If "yes" above, please indicate the approximate time lapse before underground operations are initiated:

At Once ..... Months ..... Years.....

30. Indicate the expected life of the mine (pit, etc.):

..... (Months, Years)

31. Indicate the present average rate of production (including dilution) from all ore sources on the property:

..... (tons ore/day)

32. Indicate the expected maximum rate of production from all ore sources on the property:

..... (tons ore/day)

33. Will material leaving the mine be subjected to preconcentration steps before the initial stages of comminution in the mill?

Yes ..... No .....

34. If "yes" above, indicate the type and quantity of material that will be rejected and the method of disposal of this material:

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35. Indicate all uses of water in the mine and the source and volume of water for each use:

	Source	Use	Volume Imp. Gal. Per Day
1.	.....	.....	.....
2.	.....	.....	.....
3.	.....	.....	.....
4.	.....	.....	.....
5.	.....	.....	.....
6.	.....	.....	.....
7.	.....	.....	.....
8.	.....	.....	.....
9.	.....	.....	.....
10.	.....	.....	.....

NOTE: If water in excess of 10,000 gallons per day is to be taken from other than a municipal water supply, approval is required from the Ontario Water Resources Commission, Division of Water Resources, Toronto, Ontario. (Section 28a, the OWRC Act)

36. Indicate the volume of groundwater (natural water) presently gaining access to the mine workings:

..... Imp. Gals./day

37. Indicate the total volume of water to be discharged <u>from the mine</u> during normal operations:

..... Imp. gals./day

38. Will a mill be operating on the property in conjunction with mining?

Yes ..... No .....

39. If "yes" above, will all mine (underground, open pit, etc.) water be directed to the mill for re-use?

Yes ..... No .....

40. If "no" above, indicate the proposed point of discharge for the mine water and the volume of the discharge:

Point of Discharge .....

.....

.....

.....

Volume of Discharge ..... Imp. gals./day

41. What are the chemical characteristics of the above mine water?

pH .....

SO_4 ..... ppm

Fe ..... ppm

Mn ..... ppm

.....

.....

.....

.....

Part IV

THE MILL

42. Attach a copy of the mill flow sheet. The flow sheet should indicate the points of addition of the various reagents (chemicals) that are (or will be) used.

43. Is milling in progress on the property at the present time?

Yes ..... No .....

44. If "yes" above, indicate the present rate of milling:

..... tons/day

45. What is the present (or proposed) maximum capacity of the mill?

..... tons/day

46. Indicate the type and quantity (in lbs./ton ore milled) of all reagents used in the mill:

(a) .....

(b) .....

(c) .....

(d) .....

(e) .....

(f) .....

(g) .....

(h) .....

(i) .....

(j) .....

(k) .....

(l) .....

(m) .....

(n) .....

(o) .....

47. Is the (proposed) milling circuit based on autogenous grinding:

Yes ..... No ..... Partially .....

48. If the (proposed) mill is not based on autogenous grinding, indicate the present (or expected) total rod and/or ball metal losses:

..... lbs./ton ore

49. Indicate the present (or expected) mill heads:

..... oz. Au/ton ..... % Cu ..... % U_3O_8

..... oz. Ag/ton ..... % Ni .....

.... % Zn .....

.... % Pb .....

....

....

....

50. Indicate the present (or expected) overall efficiency of the mill:

..... % recovery

Cu circuit ..... % recovery

Zn circuit ..... % recovery

Pb circuit ..... % recovery

..... circuit ..... % recovery

..... circuit ..... % recovery

51. Indicate the present (or expected) grind in the mill:

....

....

..... %-200 mesh ....

52. Indicate the amount(s) of concentrate(s) produced in the mill:

(1) ..... lbs./day (5) .....

(2) ..... lbs./day (6) .....

(3) ..... lbs./day (7) .....

(4) ..... lbs./day (8) .....

53. Indicate all uses of water in the mill; include the quantity and source of the water for each use:

	Source	Use	Volume (Imp. gals. per day)
1.	.....	.....	.....
2.	.....	.....	.....
3.	.....	.....	.....
4.	.....	.....	.....
5.	.....	.....	.....
6.	.....	.....	.....
7.	.....	.....	.....
8.	.....	.....	.....
9.	.....	.....	.....
10.	.....	.....	.....
11.	.....	.....	.....

	Source	Use	Volume (Imp. gals. per day
12.	.....	.....	.....
13.	.....	.....	.....
14.	.....	.....	.....
15.	.....	.....	.....

54. Indicate the total volume of water discharged from the mill:

..... Imp. gals./day

55. Of the above volume, indicate what quantity is returned to the mine for re-use:

All ..... None ..... Some ..... Imp. gals./day

56. Indicate the average quantity of tails (dry weight) discharged from the mill:

..... tons/day

57. What is the liquid-solid ratio of the tails leaving the mill?

.....:.....
liquid : solid

58. Are all "liquid" wastes leaving the mill being directed to the tailings area:

Yes ..... No .....

59. If "no" above, please specify:

.....

.....

.....

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.....

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.....

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60. Is the mill handling at present (will the mill handle in the future) custom lots of ore from other properties?

Yes ..... No .....

61. If "yes" above, please specify:

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62. Are tailings being recovered in the mill (or elsewhere) for use as backfill (etc.) in the mine (etc.)?

Yes ..... No .....

63. If "yes" above, please indicate (tons/day) the quantity of solid tails being recovered from the mill stream; also indicate the size fractions (% mesh) being removed:

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Part V

THE TAILINGS AREA

64. Attach a detailed scale plan drawing of the present (or proposed) tailings area. The drawing should include the following:

    (a) precise details of all retaining structures (length, width, height, materials of construction, etc.)

    (b) details of all decant (etc.) mechanisms

    (c) details with regard to the direction and route followed by the flow of wastes and/or wastewaters from the area

    (d) indications of the distance to the nearest major watercourse

    NOTE: Individual detailed large scale drawings of any facility (dam, decant system, ditch, etc.) to be constructed must be attached. Specific details with regard to the methods of construction, materials to be used, etc., are required.

65. The total area of the existing tailings basin is:

    ..... acres

66. The total area of the proposed tailings area is:

    ..... acres

67. The total capacity of the existing tailings area is:

    ..... dry tons (tails)

68. The total capacity of the proposed tailings area is:

    ..... dry tons (tails)

69. Will the present tailings area contain the entire production from the mine-mill complex for the life of the complex?

    Yes ..... No .....

70. Will the proposed tailings area contain the entire production from the mine-mill complex for the life of the complex?

Yes ..... No .....

71. If "no" above, please indicate what plans have been made for future tailings disposal on the property:

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72. Do the tailings area and all related treatment facilities lie on Company held claims?

Yes ..... No .....

73. If "no" above, indicate claim boundaries (and owners) on tailings area plan map (see question #64). Also, attach a copy of all pertinent agreements signed with the owners of the claims not held by the Company.

74. Does the present tailings area occupy a former lake basin?

Yes ..... No .....

75. If "yes" above, give the approximate size of the basin occupied by the former lake:

..... acres

76. Will the proposed tailings area engulf or otherwise disturb any existing watercourse?

Yes ..... No .....

77. If "yes" above, attach all pertinent details (name of watercourse, present average flow, direction of flow, proposed diversions, etc.).

78. Does any existing natural watercourse gain access to the existing tailings area?

Yes ..... No .....

79. If "yes" above, indicate the volume of water gaining access to the tailings area from the natural source(s) in question:

	Name of Source	Volume (Imp. gals./day)
1.	.....	.....
2.	.....	.....
3.	.....	.....
4.	.....	.....

80. Will any existing watercourse gain access to the proposed tailings area?

Yes ..... No .....

81. If "yes" above, indicate the volume of water which will gain access to the tailings area from the natural source(s) in question:

	Name of Source	Volume (Imp. gals./day)
1.	.....	.....
2.	.....	.....
3.	.....	.....
4.	.....	.....

82. Will some (or all) of the tailings area decant (or water ponded on the tailings area) be directed back to the mill for re-use?

Yes ..... No .....

83. If "yes" above, indicate the volume of water that will be directed back to the mill:

..... Imp. gals./day

84. What is the present volume of the decant overflow?

..... Imp. gals./day

85. What is the expected average volume of the decant overflow when the property is running full capacity?

..... Imp. gals./day

86. Name the first major watercourse that the decant overflow encounters as it leaves the area of Company operations:

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87. Indicate the average depth of tails in the existing tailings area:

..... feet

88. Indicate the expected average depth of tails in the tailings area after all operations on the property cease:

..... feet

89. Describe the present chemical characteristics of the tailings area decant:

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90. Describe the expected chemical characteristics of the decant from the proposed tailings area:

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91. Describe the methods of chemical treatment (reasons for, chemical addition volumes, equipment used, etc.) that are presently being used and/or will be used to control the quality of the tailings area decant (attach engineering drawings where applicable).

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92. Indicate on the tailings area plan drawing (see question #64) all sources of seepage presently encountered in the vicinity of the tailings area, the volume of each seepage flow (Imp. gals./day), and the direction of each flow.

93. Are the seepage flows from the property presently being (chemically) treated?

Yes ..... No .....

94. If "no" above, please explain:

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95. Will all tailings areas on the property be revegetated or otherwise stabilized when conventional mining-milling operations on the property cease?

Yes ..... No .....

96. If "no" above, please explain:

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THE ABATEMENT OF ACID MINE DRAINAGE IN ONTARIO

A paper presented at the Sixth Annual
Meeting of the Canadian Mineral Processors
January 22, 23, 24, 1974

This paper is intended as a review of the progress that has been made in the Province of Ontario in the field of acid drainage waste treatment technology.

Three years ago, at the Third Annual Meeting of the Canadian Mineral Processors, we presented a paper entitled "The Problem of Acid Mine Drainage in Ontario". At that time I was working for the Ontario Water Resources Commission. The paper turned out to be the very beginning of the Commission's acid mine drainage control program. In the intervening three years, the Ontario Water Resources Commission has been amalgamated with other government groups and has evolved into the present Ontario Ministry of the Environment. Today the Ministry is involved in running one of the most advanced acid mine waste control programs in the world.

As a part of its mining program, the Ontario Ministry of the Environment has published three major reports which deal directly and specifically with the industrial waste disposal problems that may arise at a mining operation. In order of publication, these reports are as follows:

(1) "The Problem of Acid Mine Drainage in the Province of Ontario".

This 338- page report covers all aspects of the problem of acid mine drainage and includes detailed sections on

acid flow detection, acid flow chemistry and acid flow treatment.

(2) "The Use, Characteristics and Toxicity of Mine-Mill Reagents in the Province of Ontario".

This report, 244 pages in length, gives the chemistry and toxicity of nearly all of the chemicals that find common use in the Canadian mining industry. Most of the toxicity figures quoted are the result of a comprehensive bioassay program that was initiated by the Ministry.

(3) "Mine Waste Control in Ontario".

This is a general report that covers such topics as:

(i) Recommended Waste Control Procedures for New Mining Operations.

(ii) Advancements in the Treatment of Acid Mine Drainage, and

(iii) A Comparison of Hydrometallurgical and Pyrometallurgical Methods of Ore Treatment as viewed from the standpoint of the Environment.

224 pages in length, this report also includes a complete copy of the Ministry's "Mineral Industries Information Sheet". This sheet, which is essentially a questionnaire designed to aid the Ministry in its assessment of mine waste treatment applications has been adopted "as is" or has been modified for use by a great number of environmental agencies that operate outside of the Province of Ontario.

Recently, after two years of work, the Ontario Ministry of the Environment published a document entitled "Effluent Guidelines and Receiving Water Quality Objectives for the Mining Industry in Ontario". This document was designed to help resolve problems associated with the mining industry in Ontario.

A limited number of the publications that I have mentioned are available from the Ontario Ministry of the Environment in Toronto.

In 1971, uncontrolled acid mine drainage was a major environmental problem in the base metal mining camps of Ontario. Today, the problem has been largely resolved. Most acid mine discharges are under control. Without the complete cooperation of the Ontario mining industry, this would have been impossible.

There are still a few properties in Ontario where uncontrolled acid drainage problems do exist but, in all cases, a program of acid abatement is underway. Most of the properties referred to are abandoned properties.

Since the purpose of this paper is to review the progress that has been made in acid mine drainage control, I would now like to briefly touch on a number of topics of general interest. Some topics are of a routine nature, others are quite controversial. I will offer my own personal opinion as to the

future of each item discussed.

(1) The Chemistry of Acid Mine Drainage

The basic chemistry of acid mine drainage has been known for well over half a century. If you are interested you will find a detailed review of acid mine drainage chemistry in the first publication of the Ministry that was mentioned. Many other texts, of course, are available.

The past three years have spawned an incredible number of technical reports concerning acid mine drainage. The most prolific source has been the Environmental Protection Agency in the United States. These reports, however, deal almost exclusively with acid problems in the American coal industry and, as such, have limited application to the Canadian base metal problems. Over the past three years, very little truly Canadian work has been published although apparently a lot of work has been done. The Environmental Protection Service of the Federal Canadian Government has been running a good-sized acid mine drainage treatment pilot plant in the Province of New Brunswick. The results of this project are expected to be significant. In addition, the Federal Canadian Government has financially encouraged the study of many critical aspects of acid mine problems. It is our understanding that the results of these studies will eventually be available to the public in some form.

Canadian or foreign, most of the acid mine drainage reports that have been published in the last three years have been of an exploratory nature and have relied heavily on information generated in past decades. Many of the available reports are simply the results of attempts to confirm old data.

Over the past three years, a handful of good reports have been produced. As such, a few new concepts were born and a few old concepts died.

The general lack of intense research into the pure chemistry and treatment of acid mine water tends to preclude the possibility of a major breakthrough in the near future. Instead, it is likely that our greatest waste treatment successes in the short-term will be achieved by making changes in our method of mining, milling and tailings disposal. It appears that a viable market for the iron sulphide minerals exists in the not-too-distant future. When this day arrives, the environmental problem of acid mine drainage at base metal operations will almost cease to exist.

(2) The Lake Disposal of Tailings

This is one topic that is always controversial. In Ontario, lake disposal of tailings is not prohibited but it is avoided whenever possible. As far as acid mine drainage is concerned, Ontario offers good evidence to support the fact

that the disposal of sulphide bearing tailings into a portion of a lake can cause serious impairment of the lake waters. There is also evidence to indicate that the disposal of less reactive tailings into a natural body of water can also cause impairment of the water.

Sometimes, it seems to be almost impossible to avoid the lake disposal of tailings. Some of the new or proposed tailings areas in Ontario cover thousands of acres and are so large that it is literally difficult to find a piece of dry land that is big enough to accommodate them. In these rare cases, the lake disposal of tailings has been permitted.

In my own opinion, it appears that the lake disposal of tailings will become completely unacceptable in the near future.

(d) Permeable vs. Impermeable Tailings Dams

In Ontario, there are no government guidelines that indicate that a tailings dam should be impermeable. In fact, tailings dams in Ontario occur in a bewildering number of shapes and sizes and exhibit all degrees of permeability and impermeability.

The trend in Ontario today is, without a doubt, towards impermeable dams when and where they are possible. The reason for this is quite obvious. Seepage from an acid

tailings area is generally highly contaminated. The seepage cannot be discharged to a natural watercourse without waste treatment. This treatment is generally quite expensive and must continue at a property 24 hours per day. In addition seepage generally continues to be a major problem for years after the property has been abandoned. Impermeable dams eliminate the seepage problem.

Since impermeable dams require more care in design and construction than do permeable dams, impermeable dams tend to be more expensive in the short term. However, when designing a tailings dam today, one should never regard the dam simply as a tailings impoundment structure. In the long term it appears that an impervious tailings dam is less trouble and less expensive than a permeable dam. It is important to note here that many serious mine waste treatment problems arise at a property not when the property is active but when it is abandoned.

In some cases, of course, the basic principles of engineering and/or economics will force the construction of permeable dams. In these cases, seepage collection and treatment systems should be inherent in the design of the dam or dams in question.

In Ontario, impermeable dams have been constructed at a number of properties as part of acid drainage control

programs. Impermeability has been achieved using clay cores, concrete cores and synthetic rubber liners.

(4) The Recovery and Impoundment of Iron Sulphide Minerals

At active and more particularly at abandoned sulphide properties, the acid drainage from the tailings area itself is the major problem. If the iron sulphide minerals were not present in an abandoned tailings area, an acid problem would not exist and long-term waste treatment would not be required. Revegetation problems would be simplified.

While it is true that, at the present time, there is no reasonable market for the iron sulphide minerals in North America, the future for iron sulphide concentrates is very bright. At the present time, iron sulphide concentrates are used as feedstock in many industrial processes in many countries around the world. Some foreign operations recover iron sulphide minerals as their main or only concentrate.

When a mining operation discards iron sulphide minerals intimately mixed with gangue to a tailings area;

(a) a non-renewable natural resource of known potential is destroyed, and

(b) in the majority of cases, acid mine drainage flows arise which

    (i) have the very real potential of impairing natural water resources,

(ii) often require extensive and expensive forms of waste treatment during both the active and abandoned phases of mining, and

(iii) generate complex and expensive revegetation problems.

There are several mining companies in Ontario today that face all of the problems that have been mentioned simply because they did not recover and separately impound iron sulphide concentrates. These companies will tell you that the lime treatment that they use today to control acid mine drainage is only a very expensive short term answer to a very long term problem. In addition, when one large mining company finds itself in control of several abandoned acid-producing properties, a serious financial problem can arise. Any company can find its competitive edge dulled by heavy waste treatment costs. In the future, public and government demands for waste treatment are going to increase, they are not going to decrease.

Today, in Ontario, there is a trend developing towards the recovery and separate impoundment of iron sulphide minerals. But the trend is not developing fast enough. It may be necessary to initiate action on this matter on a number of levels in the very near future.

(5) Wastewater Re-use at a Mining Operation

At active mine-mill operations, acid mine drainage

is more than just a problem of specific contaminants. It is a problem of volume.

The re-use of wastewater at a mining operation is a very effective way to reduce wastewater discharges from the property.

In 1971, tailings area decant re-use in the Ontario mining industry was rarely carried out. Today, largely because of the occurrence of acid mine drainage in the Province of Ontario and because of the complex mine waste control program of the Ontario Ministry of the Environment, tailings area decant re-use is quite commonly encountered.

Both the base metal sulphide mining industry and the iron mining industry have engineered great advances in the concepts of wastewater re-use. For very real technical reasons, the gold industry and the uranium industry have not yet been able to employ tailings area decant wastewater re-use to any great extent although high degrees of wastewater re-use within the mills are practised.

During 1973, a great many problems were encountered with base metal sulphide decant recycle systems in Ontario. However, most problems were of a local nature and could only be solved by the company that was experiencing the problem. In most cases the problems were adequately solved or a solution was known.

It was determined in 1973 that most of the recycle problems encountered resulted from the failure of many of the companies involved to adequately age their effluents before recycle. Serious problems arose when some companies attempted to recycle wastes directly from within the tailings area itself. At this point, it was found that the wastes generally were not sufficiently aged and also, slime concentrations were high.

In 1973, it became common practice in Ontario to direct decant wastes to one or more downstream settling ponds before recycle was attempted. It now appears that the downstream ponds are necessary in nearly every case.

At the present time, the mining guidelines of Ontario read as follows:

"The mine-mill Effluent Guidelines of the Ontario Ministry of the Environment will be influenced by positive mine-mill waste treatment practices such as wastewater re-use".

At the present time, wherever wastewater re-use is technically and scientifically supportable, the expectation is that it will be carried out.

It is probable that wastewater recycle will be mandatory sometime in the future.

(6) Mandatory Bonds for Mine Waste Revegetation

There is a prevalent public feeling in North America that mining companies should be required to post pre-operational bonds in order to ensure the adequate reclamation of abandoned mining lands.

The areas to be reclaimed include the following:

(a) abandoned tailings areas and tailings dams etc.

(b) abandoned rock dumps etc.

(c) abandoned open pit mine workings etc., and

(d) abandoned mill areas (buildings etc.)

It appears that there are basically two ways to set up a bonding system. One way would be on a "cost per area" basis. The other way would be on a "cost per ton" basis. At the present time most environmental agencies appear to favour the "cost per area" basis while most segments of the mining industry appear to favour the "cost per ton" basis.

At present day rates, the "cost per acre" approach would involve a bond of approximately 500 to 1,000 dollars per acre of tailings. The "cost per ton" approach would involve a charge to the company of approximately 1 cent per dry ton of tailings discharged. Additional charges would have to be made for the reclamation of waste rock dumps and abandoned mine workings etc., if such reclamation is required.

Mandatory bonding, of course, is a very unpopular topic. Its prime purpose is to ensure the rehabillitation of derelict mining land. Its side effects, however, could include the elimination of marginal mining companies and the diversion of exploration and development funds elsewhere.

It appears that, to a greater and greater extent, environmental factors are determining whether or not an interesting mass of rock is ore or simply waste. The environmental factors of today will not disappear from the scene. They will become more and more important. The mining company that incorporates environmental planning in its design functions today, will become the successful company of the future. The company that ignores environmental planning today, will cease to exist.

In my opinion, mandatory bonds for mine waste reclamation will be a reality in the future.

(7) Problems with the Present-Day Treatment of Acid Mine Drainage

Technically speaking, the presently-used chemical treatment of acid mine drainage is, at best, a short term answer to a long term problem. Three years ago, many uncontrolled acid flows existed in the Province. Today, nearly all such flows are subject to lime treatment with its attendant paraphernalia. In a few cases, other treatment reagents and systems are use.

On a day-to-day basis, lime treatment, when properly handled, yields an effluent that exhibits an acceptable pH and generally acceptable metal concentrations. Lime treatment does, however, act to increase the hardness and total dissolved solids content of the final discharge and has little effect on substances such as ammonia. In addition, lime treatment does, on occasion, produce voluminous masses of sludge which in itself constitutes a waste disposal problem.

It appears that the emphasis today must be placed on those methods of acid mine drainage control that result in long term solutions to the problem and yet do not involve massive treatment reagent additions. Such methods include:

(a) iron sulphide segregation

(b) wastewater recycle

(c) the construction of impermeable tailings dams

(d) the revegetation of derelict mining lands, and

(e) the mechanical aeration of oxidizable wastes.

(8) <u>The Occurrence of Unstable Sulphur Compounds in Mine-Mill Effluents</u>

In sulphide mill operations, unstable sulphur compounds are generated when alkaline solutions come into contact with sulphide minerals. Under appropriate conditions, these unstable sulphur compounds will oxidize to form sulphuric acid.

It has been stated that the rate of dissolution of sulphide ions from ore particles is proportional to the alkalinity of the milling water, the length of time the ore particles are exposed to high pH in the mills, the water temperature and the degree of agitation. It has also been stated that when the pH, agitation and water temperature are held approximately constant, greater concentrations of unstable sulphur compounds will result as the period of exposure of mill water to ore is lengthened. It seems to follow, therefore, that if tailings area decant recycle is employed at a sulphide property, the buildup of unstable sulphur compounds in the recycle water is a possibility since each time the water is recycled it is re-exposed to the reactive ore.

In Ontario, the presence of unstable sulphur compounds in recycle water systems has created local problems. Since natural oxidation is the only relatively successful method that is presently available for the large scale treatment of the compounds in question, sulphur-oxidation ponds have become common in the Province of Ontario. Retention times of between 30 days and 1 year have been employed. Conceivably, mechanical aeration could dramatically reduce the retention times involved and could also solve the overall problem of residual reagent concentrations in final effluents and in recycle lines.

The main problem with the oxidation pond concept is that the ponds do not appear to work well during the cold winter months.

There is one important point to remember. If an oxidation pond works successfully, the effluent from the pond will tend to be acid. If accidity develops, the acidity should be neutralized before discharge to a natural watercourse.

Conclusion

The acid drainage control program in Ontario over the past three years has been highly successful. Most short term problems have been solved. Long term solutions are being developed.

Existing unsolved problems that form part of the acid mine drainage situation include:

(a) the control of ammonia

(b) the control of nitrogen compounds other than ammonia and

(c) the control of total dissolved solids and hardness.

A great amount of work is still required relative to:

(a) the revegetation of acid derelict mining lands

(b) the perfection of wastewater recycle systems

(c) iron sulphide recovery and segregation, and

(d) the development of waste treatment concepts that do not involve massive reagent additions.

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